The Nature and Origin of Saline Groundwater in the Wairau Valley, Marlborough, New Zealand.

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submitted in partial fulfilment

of the requirements for the degree

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By

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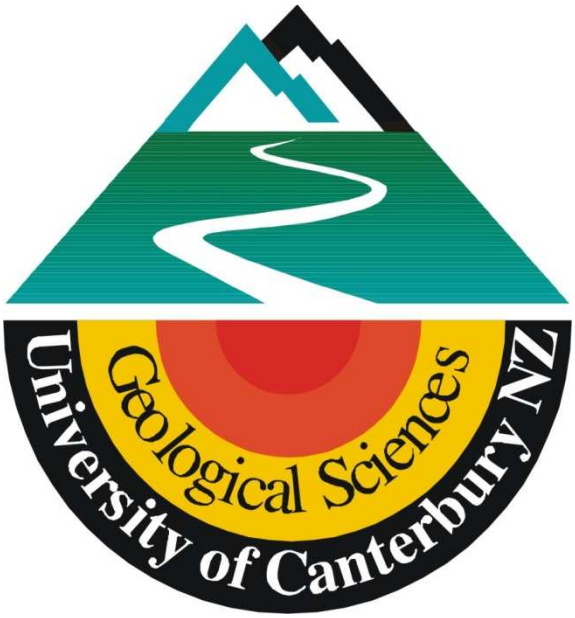

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ABSTRACT

In the Wairau Valley 40 km southwest of Blenheim, elevated salinities are present in the groundwater below a depth of approximately 15 m, to the north of the Wairau Fault. Saline water is present very close to the surface between the Southern Hills and the Wairau Fault. Highest concentrations are located in well O28/w/0219 with total dissolved solids concentrations approximately 31,000 mg/L. Only a few wells in the study area have intercepted the saline groundwater. A report by Taylor (2003) has identified the groundwater below the Holocene terrace surface is recharged from Southern Hills runoff, however the Wairau Fault has a significant impact on the groundwater flow on the south bank acting as a semi-permeable barrier to groundwater flow from the southern Hills streams identified by several spring which emerge on the fault trace.

The scope of this investigation was to identify the extent of the saline groundwater in the Homelands area and to attempt to define the origin of the highly saline groundwater. Furthermore, to define the groundwater flow path below the upper terrace surface to recharge the Wairau Valley Aquifer.

The Multi-Electrode Resistivity technique was used to define the extent of the saline groundwater. This shows the saline groundwater is ubiquitous at depth in the study area. The depth to the freshwater/saline water interface varies laterally in the resistivity profiles. A major control on the presence of the groundwater salinity is considered to be the permeability of the gravel. Gravels with a higher permeability are probably washed of any residual salinity that may have been present in the past.

Investigations into the origins of the saline groundwater were completed using stable isotope analysis (^{18}O, ^{2}H, and ^{13}C), hydrochemistry and age dating techniques (^{3}H and ^{14}C). Due to the complex chemistry a single source could not be identified, however two methods were identified as the most likely. This was evaporative concentration of fresh water in the Wairau Valley, or the upward migration from the Wairau Fault of formation water probably of seawater origin. The stable isotope data fits best with an evaporative concentration of freshwater within the Wairau Valley, however, ratios of chemical constituents are very similar to other formation waters found in other parts of the world.

Stream gauging of streams on the south bank show no significant water loss in the reaches north of the Wairau Fault. Therefore, recharge must be crossing the Fault trace as groundwater. Boundary Creek looses all of its surface flow for most of the year upon reaching the valley floor. Bounday Creek has washed out sections of the Wairau Fault and Major terrace riser between Wr 1 and Wr 2 terrace surfaces. It is proposed that groundwater flowing in the gravels reworked by Boundary Creek is the major recharge source for the Wairau Valley Aquifer.

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CHAPTER ONE

INTRODUCTION

1.1 Project Background

The Wairau Valley Aquifer system provides groundwater resources for residential, industrial and agricultural/horticultural uses in the lower part of the Wairau Valley near Blenheim. Further up the valley near the Wairau Valley Township, a significant salinity anomaly has been identified by Marlborough District Council monitoring. From limited data, generally the anomaly appears to be at depths greater than 15 m, however, this is highly variable and not consistently present at this depth. Some shallow wells close to the Wairau Fault trace show elevated salinity.

Elevated conductivity is present at the surface in one area between the Wairau Fault trace and the Southern Hills. Unusually high values of chloride (>3000 mg/L) are also associated with elevated arsenic, boron, sodium, calcium, magnesium, manganese, and bromide in several wells that have been drilled close to the main fault trace. Various investigations have been undertaken, although to date these have really only defined the problem without satisfactorily establishing key parameters and the reasons for elevated chloride, and other ions, well above other waters in the study area.

1.2 Project Objectives

Previous studies have identified Southern Hills water as the recharge source for the Wairau Valley Aquifer below the Holocene terrace surface. However, the Speargrass gravels which fill the valley have been shown to be relatively tight and the Wairau Fault has also been identified as a barrier to groundwater movement. This thesis attempts to define the groundwater system of the Southern Hills groundwater and determine the origins and extent of the saline water through the collation of existing data in the Marlborough District Council database together with the collection and interpretation of new data. The foremost objectives are to:

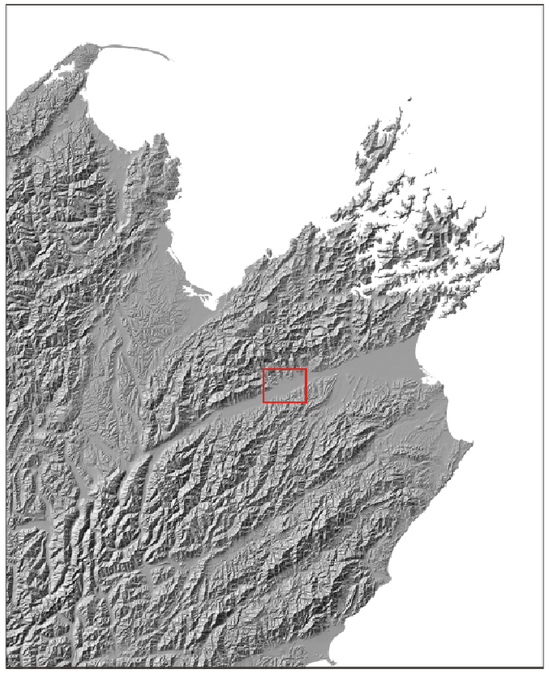
- Identify the origin and age of the high salinity present.

- Define the subsurface extent of the saline water, establish a three dimensional model of the subsurface salinity profile across the Wairau Fault.

- Define the nature of the complex groundwater flow pattern on the south bank and define mechanisms for groundwater flow across the fault.

1.3 Study Area

The Wairau Valley is located in the Marlborough region of the South Island of New Zealand. The field area is located on the south bank of the Wairau River approximately 40 km inland from Blenheim. The study area boundaries are defined by Church Lane in the east and Boundary Creek in the west. Northern and southern margins are defined by the Wairau River and the Southern Hills respectively (Figure 1.1). The study area is approximately 24 km^2 and is generally constrained to the valley floor. Within the study area, the major focus of investigations is around Mill Road and Parsons Road.



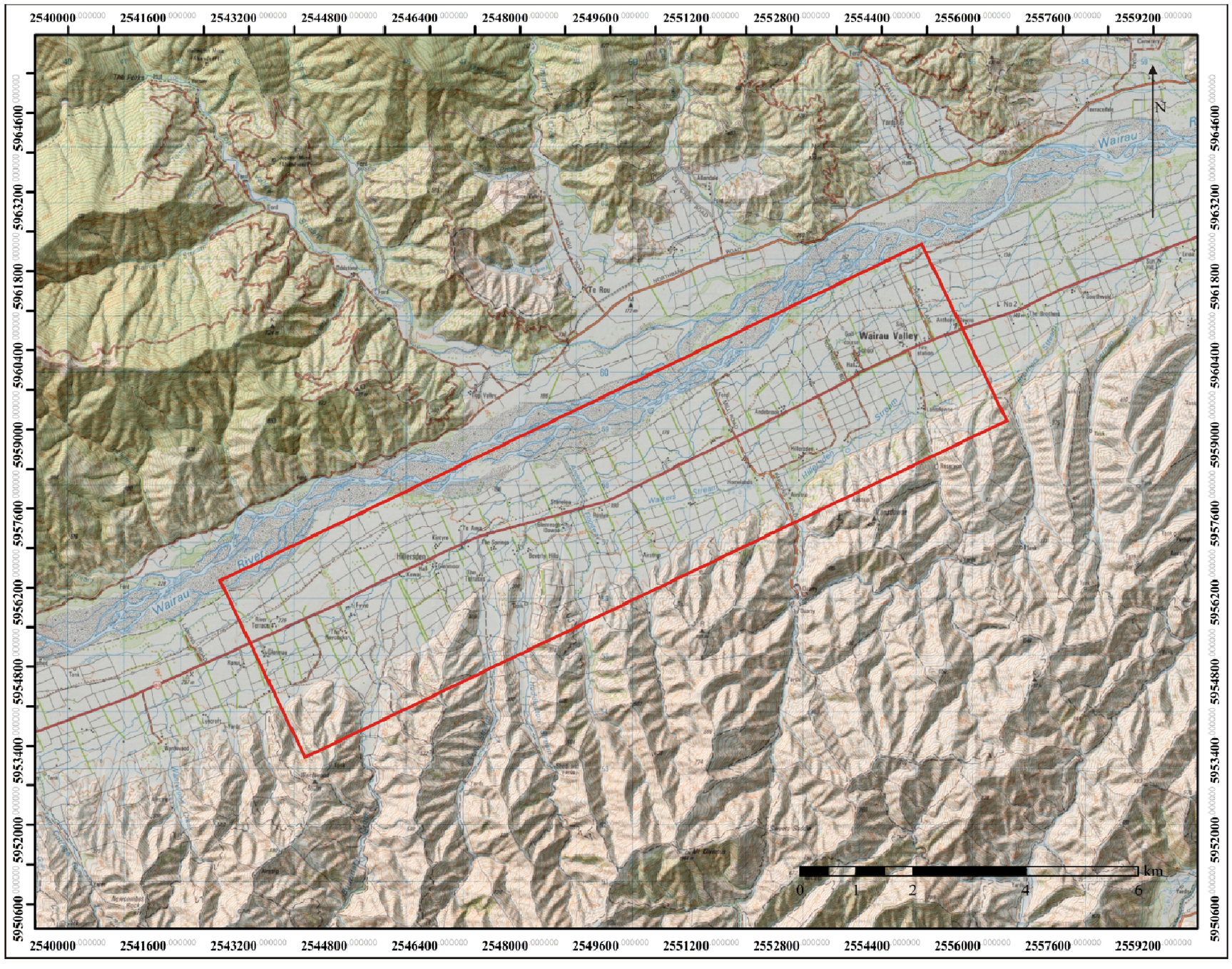


Figure 1.1: Location of the study area.

1.4 Physiography

1.4.1 Climate

Climate data, including wind direction, precipitation, and temperature is collated into Appendix 1.1. Relatively little climate data has been collected for the Central Wairau Valley.

Precipitation gradients in the Wairau Valley show significant variation over relatively short distances (Figure 1.2). This is due to the topographic relief of the ranges surrounding the valley. The Richmond ranges north of the Wairau Valley provide good protection from westerly and north westerly air streams, which are predominantly the direction of major cold fronts. Precipitation in the Richmond Ranges close to the study area is approximately 2,400 mm/year compared to just under 1,000 mm/year on the valley floor. The Southern Hills catchments, adjacent to the study area, receive only slightly more than the valley floor, approximately between 900 and 1,200 mm/year. This is due to the rain shadow effect from the Richmond Ranges and the lower relief of the Southern Hills.

The predominant wind in the Wairau Valley is the south westerly travelling up the valley. This is relatively consistent throughout the year, however, the strongest winds occur in January and February and these are generally much stronger than other months.

The highest average temperature occurs in January (17.4^{o}C) with the coolest month being July (4.4^{o}C). No data is available on the sunshine hours for the Wairau Valley, however, Blenheim and Nelson both show yearly sunshine hours of 2405 and 2409 respectively. Values in the Wairau Valley are probably similar. There is no data for evapotranspiration rates in the Wairau Valley.

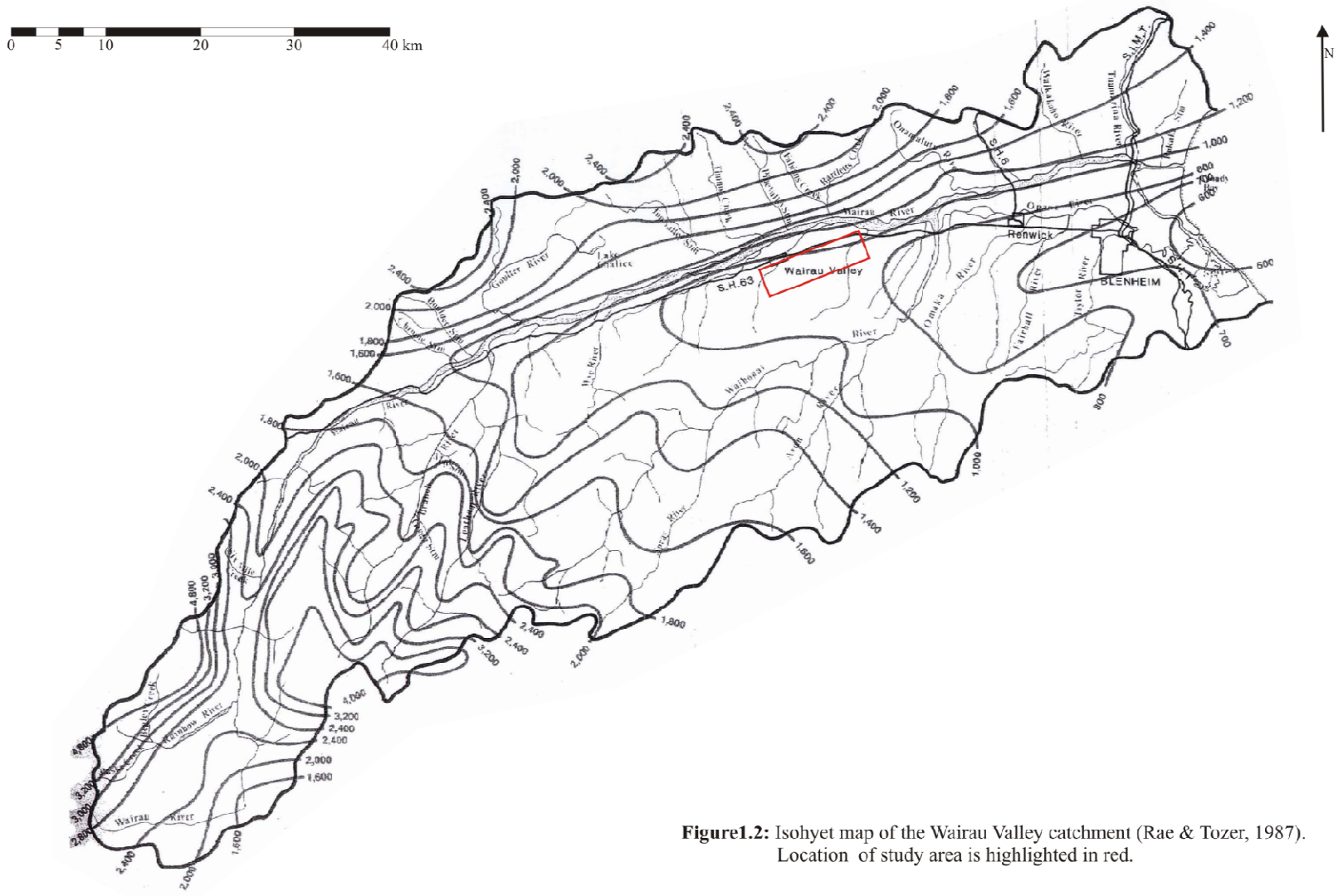


Figure1.2: Isohyet map of the Wairau Valley catchment (Rae & Tozer, 1987). Location of study area is highlighted in red.

1.4.2 Vegetation and Landuse

Prior to colonisation, the south bank of the Wairau River and the Southern Hills were covered by dry land forest and shrub land. Common flora types include; tussock grassland, tree broom, Kowhai, Kanuka, matai, and totara (Rae & Tozer, 1988). The present day landscape is dominated by exotic grassland for sheep and cattle farming. There have been attempts to convert some areas for viticulture, however, the elevated salinity close to the Southern Hills is not favourable to vine growth. No vineyards are presently operating in the study area.

1.4.3 Soils

Soils for the Wairau Valley are described from Rae & Tozer (1990). Soils in the study area consist of dark brown stony silt topsoils which overlie a dark yellowish brown very stony silt loam subsoils. Below this layer consists of a brown very stony coarse sand substrate. These descriptions reflect a poor quality soil for agriculture.

1.4.4 Geomorphology

The geomorphology of the south bank is dominated by a fluvial environment. The south bank in the study area consists of two major terrace surfaces, Wr1 and Wr2 (Figure 1.3). The terrace surfaces have been significantly degraded and reworked and gentle undulations of old river channels dominate the geomorphic expression on each surface. The terrace riser between these two surfaces accounts for almost all of the change in elevation between the Wairau River and the Southern Hills.

The trace of the Wairau Fault is visible in sections within the study area, however, in some parts it has been completely eroded from subsequent fluvial processes. Just west of Parsons Road, in between the Southern Hills and the Wairau Fault, is a topographic low which collects runoff during rainfall events and is the only area to show elevated conductivities at the surface. In the same location minor features are visible as highly eroded mounds on the terrace surface. These correlate well with an eroded scarp on the northern block of the Wairau Fault.

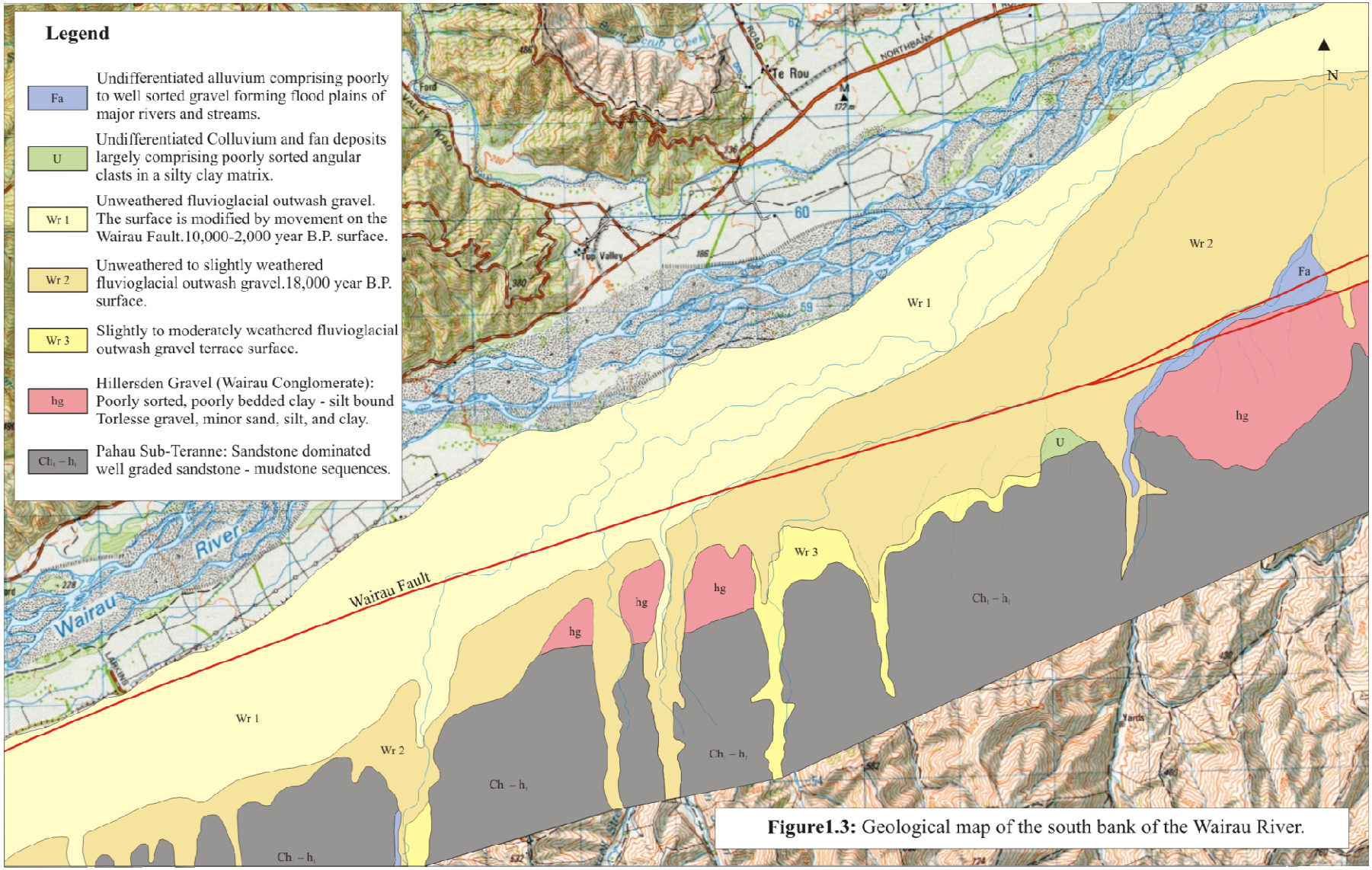


Figure1.3: Geological map of the south bank of the Wairau River.

1.5 Geological Setting

1.5.1 Structural Development

New Zealand is located on an obliquely convergent plate boundary between the Pacific and Australian plates (Figure 1.4). The Marlborough Fault System (MFS) represents the transition zone between oblique convergence and subduction of the Pacific plate beneath the Australian plate in the north, and the dextral reverse oblique slip due to oblique collision in the south (Zachariasen *et al.*, 2006). The MFS is a series of major right-lateral strike-slip transcurrent faults which form a series of large northwest tilted blocks between the fault controlled valleys (Brown, 1981). The most prominent active faults in the MFS include (from northwest to southeast) Wairau, Awatere, Clarence, Kekerengu, and Hope Faults. All of these faults trend northwest, approximately parallel to the Pacific-Australian relative plate motion vector (Van Dissen & Yeats, 1991).

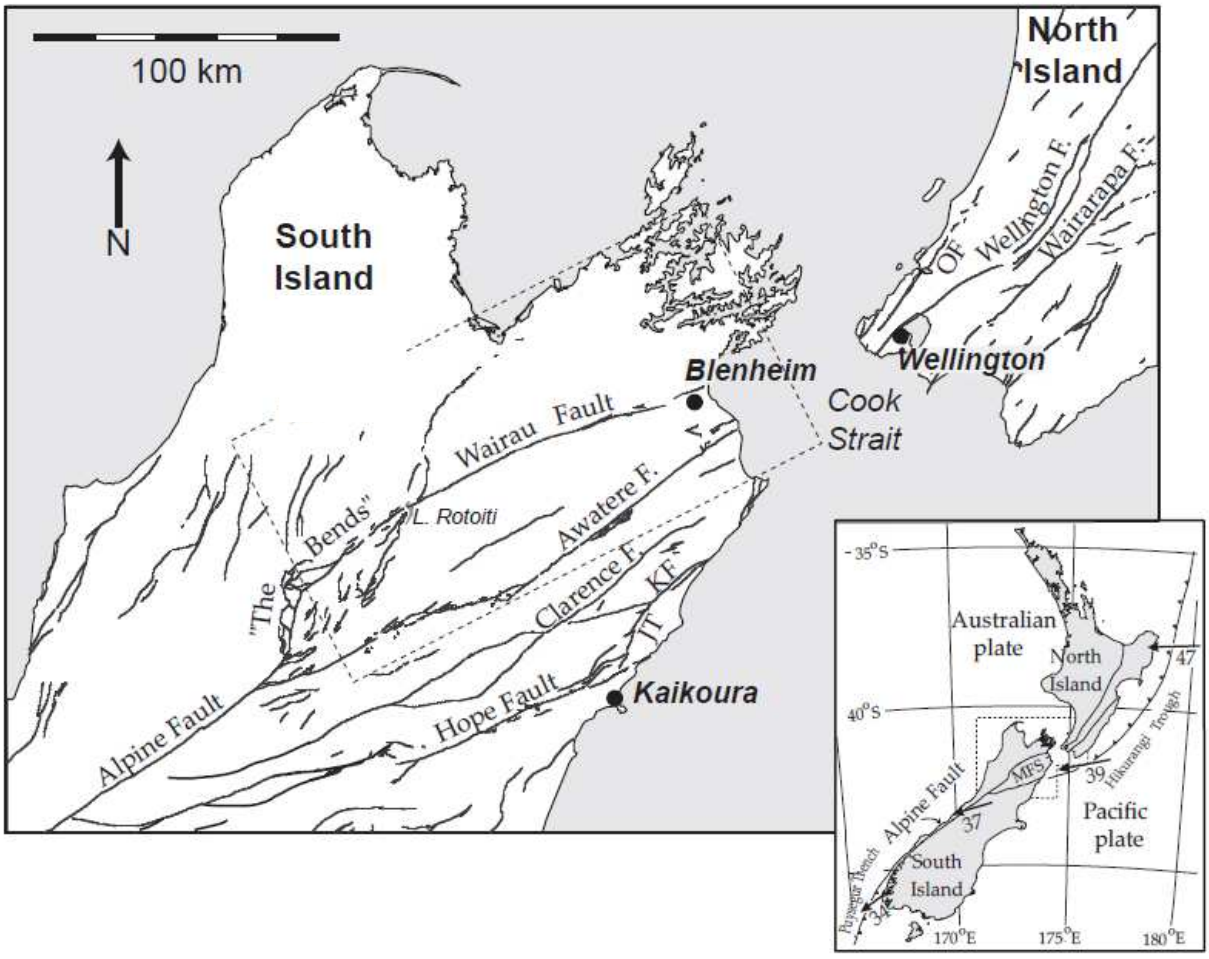


Figure 1.4: Structural Setting of the Marlborough Fault System (Zachariasen *et al.*, 2006).

1.5.1.1 Wairau Fault

The Wairau Fault is the north eastern continuation of the Alpine Fault from Lake Rotoiti, extending the length of the Wairau Valley onto the Wairau Plains and offshore into Cloudy Bay (Figure 1.4).

In the Upper Wairau Valley the fault trace has a distinct northeast trend visible in sections where modern fluvial processes have not eroded the scarp. Six kilometres northeast of Hillersden the Wairau Fault bifurcates into two distinct traces. The northern strand enters the Wairau River Bed at Black Valley Stream. This strand is thought to be discontinuous and it may adjoin the Bedford Road traces (Lensen, 1976). The southern trace cuts into the Southern Hills and out across farmland west of the Waihopai River towards Renwick. Grapes & Wellman (1986) mapped the southern strand of the Wairau fault, east of Renwick, where it is a single trace to within four kilometres from the coast. Little is known about the presence of the fault offshore. Several Studies have suggested it continues north west to just offshore of the Kapiti Coast (Zachariasen *et al.,* 2006), but marine studies suggest that it links with the major southern North Island faults such as the Ohariu Fault (Kingma, 1974; Stevens, 1974; Carter *et al*., 1988; Begg & Johnston, 2000).

The Wairau Fault has an average slip rate of 3-5mm/yr with single event displacements of 5-7 m. The most recent surface rupture is thought to have occurred between 1811-2301 years B.P., and the penultimate to have occurred approximately 2680+/-60 years B.P. with an average recurrence interval to be about 1150-1400 years (Zachariasen *et al.,* 2006).

1.5.2 Stratigraphy

1.5.2.1 Torlesse Terrane

Torlesse Terrane (Figure 1.3) forms the basement rock in the field area. Torlesse lithologies are dominated by massive sandstones, interbedded fine sandstones and mudstones, with rare volcanics, red cherts, and limestone present. South of the Wairau Fault, Late Jurassic to early Cretaceous Pahau sub-terrane forms the Southern Hills of the Wairau Valley. North of the Wairau Fault Permian to late Triassic Rakaia sub-terrane is present as a relatively thin wedge before the Caples Terrane forms the basement of the Richmond Ranges north of the Wairau Valley (Rattenbury *et al.*, 1998).

1.5.2.2 Wairau Conglomerate

Resting unconformably on Jurassic Torlesse, the Wairau Conglomerate is found at the eastern end of Cloudy Bay and as far west as Hillersden in the Wairau Valley. The conglomerate is approximately 400 m thick consisting of three divisions. A coarse basal layer of poorly rounded boulders Torlesse in origin, a layer approximately 240 m thick of conglomerate thought to be shallow marine depositional setting, and a gradational change into a fluvial depositional environment in the upper 120 m. Within the unit none of the detrital material is derived from the north of the Wairau Fault indicating that deposition is prior to the main movement of the Alpine Fault (Branch & Dagger, 1934). The Wairau Conglomerate is middle Miocene in age and slightly younger than the Great Marlborough Conglomerate found in the region. The Wairau Conglomerate is overlain unconformably by Pleistocene and recent gravels (Rattenberry *et al*., 1998; Begg & Johnston, 2000).

1.5.2.3 Pleistocene Gravels

The 2 earliest known outwash gravels in the Wairau Valley are the Manuka and Tophouse Formations, which correlate to the Waimaunga and Waimea Glaciations respectively (Suggate, 1965). The Tophouse Formation consists of highly weathered, poorly sorted sub-angular to sub-rounded gravel with blocks up to 1 m in diameter. It is thought to have filled the valley from the Tophouse area and subsequently eroded away during interglacial periods. The Manuka Formation is very similar to the Tophouse, differentiation is based on the Manuka Formation having a thicker loess cover and the surface being more dissected. The gravel and sand also has a greater degree of weathering in the Manuka formation (Brown, 1981).

The Speargrass Formation is glacial outwash gravel of the Otira Galciation (Last Glacial Maximum). Lensen (1976) mapped the Wairau Fault in the Hillersden area as offsetting the late Otiran stage degradation surface (c.18 000 ka). Speargrass gravel is associated with poorly sorted fluvial deposits of gravel, sand, and clay. Clasts are relatively unweathered with a blue-grey colour. Distinguishing features from younger deposits are is the lower permeability reflecting a greater proportion of fines in the matrix. When drilling Speargrass gravels they were found to be much tighter than the postglacial fluvial deposits. The Speargrass Formation gravels can be distinguished from the Tophouse gravels by the degree of weathering of clasts. Tophouse gravels

are brown in colour, which is representative of the degree of weathering compared to the blue Speargrass gravels (Brown, 1981).

1.6 Previous Work

There is only one unpublished report that covers some aspects of the saline water in the Wairau Valley. The report completed by Taylor (2003) for the Marlborough District Council analysed isotope and chemistry of south bank wells and streams to determine the groundwater recharge source. This included several moderately saline wells close to the fault trace. This report postulated a Torlesse derived connate seawater source migrating up fault and mixing with old Wairau River water. Taylor (2003) also defined the lower terrace groundwater to be derived from Southern Hills runoff and not Wairau River water as had been previously suggested. Several other unpublished reports on the nature of the south bank hydrological system have been competed by the Marlborough District Council.

Due to the proposed hydro power scheme in the Wairau Valley several reports by various consultancies for consent applications have been completed. Many papers have been published on the Wairau Fault, however, they have generally focused more on the Upper Valley (Branch & Dagger, 1934; Lensen, 1968) and on the Wairau Plains (Grapes & Wellman, 1986). The length of the Alpine Fault, including the Wairau Fault has been mapped by Lensen (1976) and Berryman, *et al*., (1992). Zachariasen *et al*., (2006) trenched across the trace of the Wairau Fault in the study area to identify and date past movements and further constrain the slip rate. Lensen (1976) mapped the terrace surfaces in the Hillersden area, Brown (1981) describes the gravel units within the Wairau Valley and onto the Wairau Plain. Eden (1983) completed a PhD on the Late Quaternary history of the Wairau and Awatere valleys. No geophysical surveys have been completed within the study area prior to this investigation.

1.7 Research Methods

During the initial fieldwork, logging of the extension of well O28w/0219 to 50 m depth during April 2007 was completed. This provided critical data on the nature of the valley gravels and a depth profile of the variation in conductivity and static water levels. The bore log of O28w/0219 was important as ground control for the resistivity surveys completed for this investigation. Groundwater samples were collected for hydrochemical analysis as well as stable isotope ratios

($\delta^{18}O$, δD, $\delta^{13}C$) and radioactive isotope (^{3}H, $\delta^{14}C$) analysis to define the age and source of the saline water. The data collected from O28w/0219 is interpreted with well and stream samples in the study area from the Marlborough District Council database. In August 2007, a stream gauging survey was completed along the south bank streams to identify surface water loss to the groundwater system as potential recharge for the Wairau Valley Aquifer, and to determine the surface water imbalance either side of the Wairau Fault. Aerial photo interpretation and surface mapping were used to identify important surface features which may influence the hydrological system. For example, the location of springs and their relationship to the Wairau Fault. During October 2007 and April 2008 two resistivity surveys were completed to define the subsurface model for the saline groundwater in the study area. Prior to this study all that was known about the saline groundwater was derived from only a few wells in the area. Three resistivity surveys parallel to Mill Road and Parsons Road aim to define the extent of the saline water laterally and at depth, and to better understand the shallow groundwater flow on the south bank.

1.8 Thesis Format

The thesis is presented in seven chapters. Chapter Two defines the hydrostratographic model and introduces aquifer properties related to groundwater flow and the nature of the Wairau Valley gravels. Chapter Three presents the geophysical data collected in this investigation. Chapter Four introduces and discusses the isotope analysis. Chapter Five presents the water chemistry data analysis of the saline wells and their relationship to Southern Hills runoff and Wairau River water. Chapter Six builds on the analysis presented in Chapters Two through Five and discusses all the data with respect to the major objectives of the investigation. Chapter Seven summarises Chapters Two through Six and suggests future work.

CHAPTER TWO

HYDROGEOLOGY

2.1 Introduction

Chapter two introduces the hydrological setting of the study area. Aquifer properties are discussed including transmissivity of the units within the study area. Clast lithology for the gravel units at varying depths is analysed with specific reference their potential influence on the water chemistry. Surface water characteristics are discussed and the implications for groundwater movement on the south bank of the Wairau River.

2.2 Hydrostratigraphy

2.2.1 Subsurface Investigation

In April 2007 observation well O28w/0219 (Figure 2.1) was extended from 15 m to 50 m for exploratory purposes. Aims included defining the thickness of the Wairau Valley Aquifer at Mill Road and to determine the depth to saline water. On completion of drilling, water samples were collected for hydrochemical, stable isotope, and age dating analysis.

Figure 2.2 contains the lithological log, conductivity with depth, and static water levels with depth for well O28w/0219. The upper 20 m of the lithological log is sourced from MDC Driller logs. Between 20-35 m the sample descriptions were completed on Site, below 35 m samples were collected by the driller every meter or where a noticeable change in lithology occurred and later logged. Electrical conductivity readings were taken at two meter intervals beginning at 14 m to develop a profile of the variation in conductivity with depth.

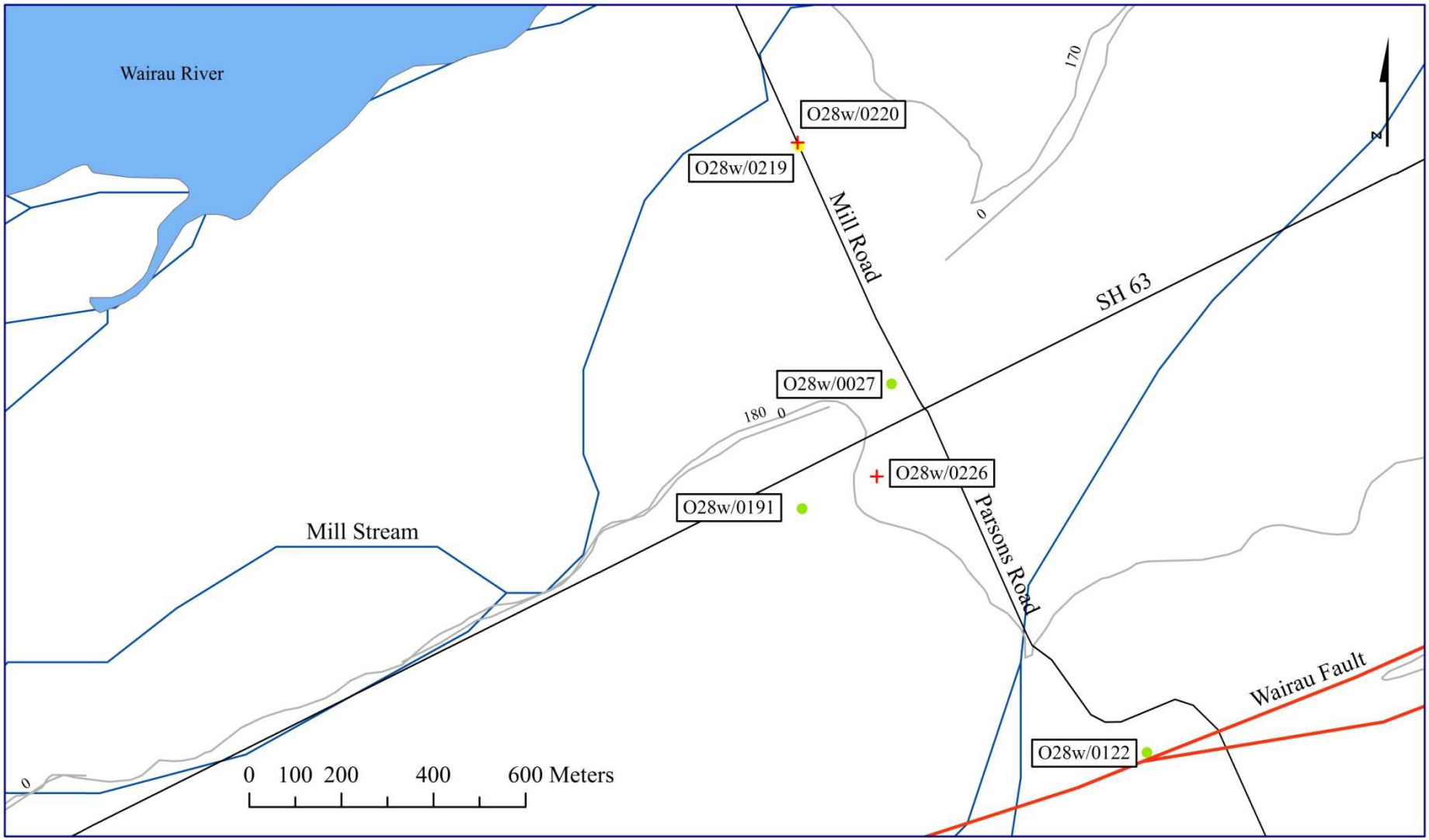


Figure 2.1: Location of selected wells in the study area. Red crosses represent the pumping wells for the two aquifer tests, dots represent observation wells,

The lithological log shows two distinct units. They are differentiated by lithology and water bearing capacity and have a significant control on the salinity of the groundwater.

Approximately the upper 18 m of the log consists of water bearing gravels. Two sand layers are present at 15 m and 17 m which are probably laterally discontinuous. The gravels are relatively clean with minor clay content. As a result these gravels have a high water yield relative to other units in the study area. This layer is interpreted as reworked gravels of Speargrass origin. As the Wairau River avulsed across its present flood plain the river redistributed the gravels resulting in removal of fines present in the older gravel. The resulting deposit is clean gravel with only a minor clay and fine sand component and define the approximate depth of the Wairau Valley Aquifer in O28w/0219.

Below 18 m the gravels become significantly tighter and more difficult to drill. There is a slight variation described in the log, but changes are very minor. Below approximately 18 m to a minimum of 50 m the lithology is interpreted as the Speargrass Formation outwash gravels. As described in Chapter One the Speargrass Gravels are generally blue-grey with a significant amount of clay and fines in the matrix. The Tophouse and Manuka Formations are characterised by highly weathered gravels. At the maximum depth of drilling un-weathered, blue-grey gravels still dominated the collected samples, therefore, the Speargrass Formation has a minimum depth of 50 m in the valley. The sample variation throughout the bore log is attributed to the aggradational setting and variation in fluvial processes on the floodplain during deposition. None of the individual layers visible in the log are thought to be laterally continuous.

Between the depths of 14 m and 16 m there is a sharp increase in the conductivity of the groundwater (Figure 2.2b). Shallower than 14 m, conductivity values are less than 300 mS/m, but when measured again at 16 m the groundwater conductivity had risen to greater than 3000 mS/m. This suggests that elevated conductivity could occur within reworked gravels that defines the Wairau Valley Aquifer or this may reflect the change to Speargrass gravels. A pump test at O28w/0220 showed no fluctuation in conductivity readings of the discharge over a 47 hour period. Well O28w/0220 has a screen from 10 m to 12 m depth, this is only 4 m above the depth that high conductivity values were measured. The higher conductivity values between 16 m and 20 m could represent mixing at the base of the Wairau Valley Aquifer between the

fresh Southern Hills water of The Wairau Valley Aquifer and saline water seepage from the tighter Speargrass Gravels below. During pumping the increased salinity would be rapidly diluted by fresh water flowing laterally from the more permeable gravels of the Wairau Valley Aquifer. The low hydraulic conductivity of the Speargrass Gravels precludes any significant contribution of saline water to be drawn up at a fast enough rate. Another possibility is that the boundary between the reworked gravels and the Speargrass Gravels is closer to 15 m depth. Sand layers at 15 m and 17 m are more likely to be within the Speargrass Gravels than reworked gravels, however, the driller noted a water bearing layer is present between the two sand layers. From 16 m to 25 m conductivity values were between 3000 mS/m to 4500 mS/m, this represents conductivities only slightly less than seawater. Below 25 m conductivities are above 5000 mS/m showing only minor fluctuations to 50 m depth. The conductivities between 16 m and 25 m is possibly a result of fresh water seepage from the Wairau Valley Aquifer into the Speargrass Gravels, below 25 m groundwater is possibly close to maximum salinity for Wairau Valley waters.

At the start of each day of drilling, the static water level was measured by the driller to give a profile of the variation in the static water levels with depth (Figure 2.2c). There is an approximate drop in the static water level of 1.5 m at the base of the Wairau Valley Aquifer to the final depth of the well (50 m). This suggests a downward flow gradient in the gravel i.e. gravity drainage. The opposite would be expected if deep saline water was migrating upward along the Wairau Fault. However, due to the high variability of the fluvial deposits the profile here may not be representative of the entire deep valley gravels (MDC Groundwater Group, 2007).

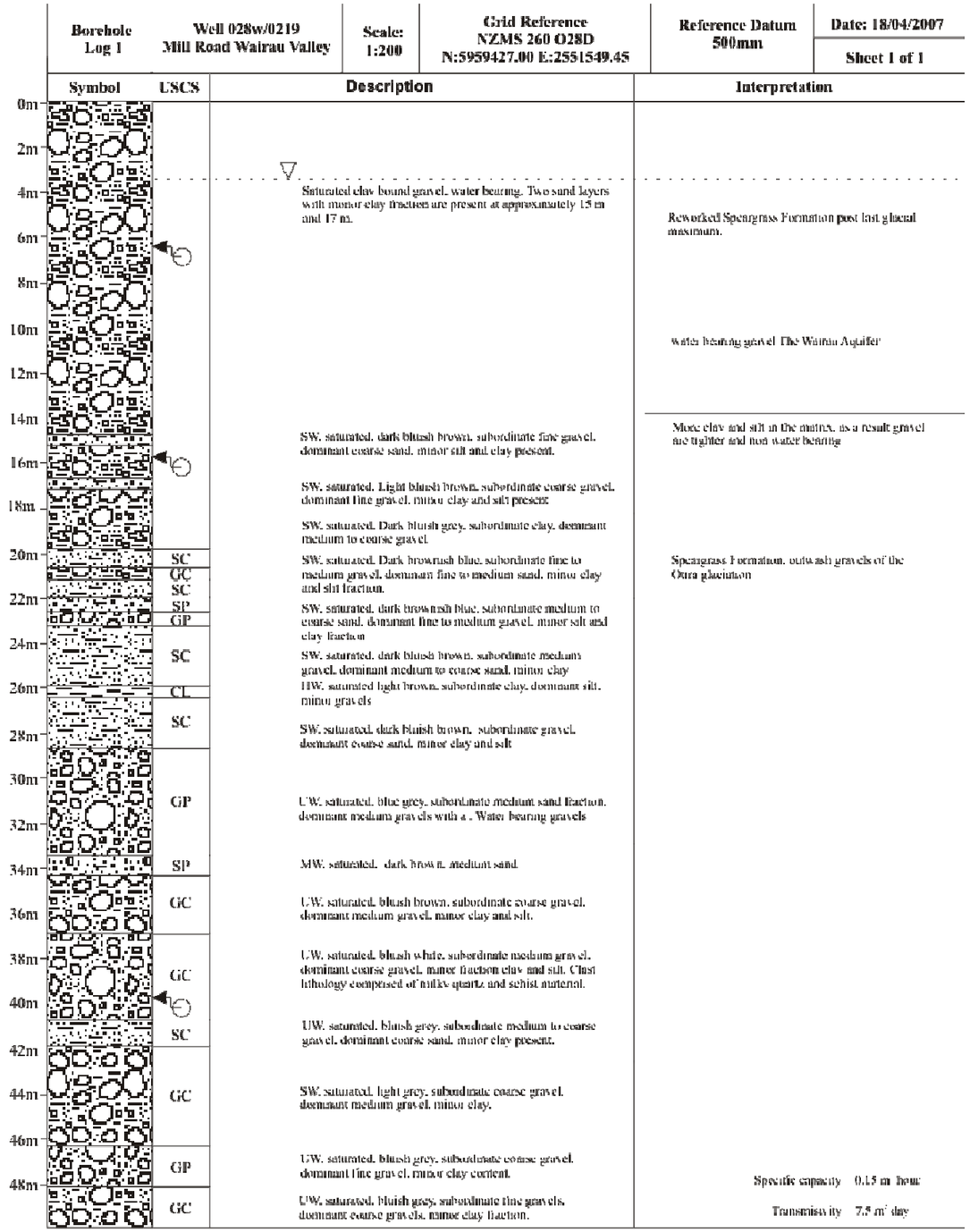


Figure 2.2a: Lithological Bore Log of O28w/0219

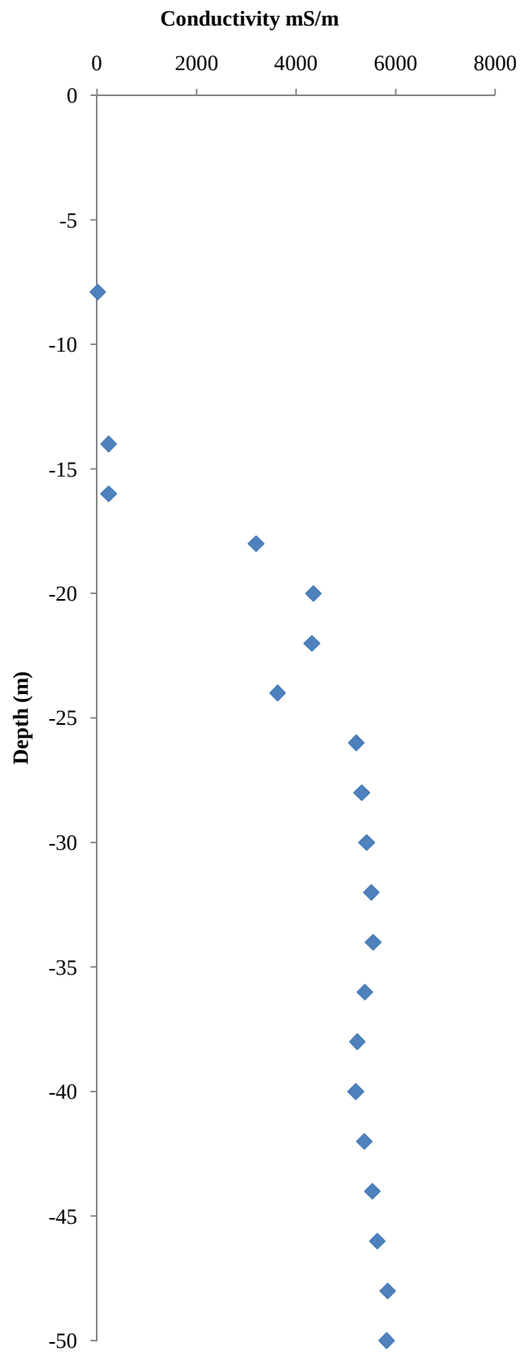


Figure 2.2b: Conductivity with depth for O28w/0219

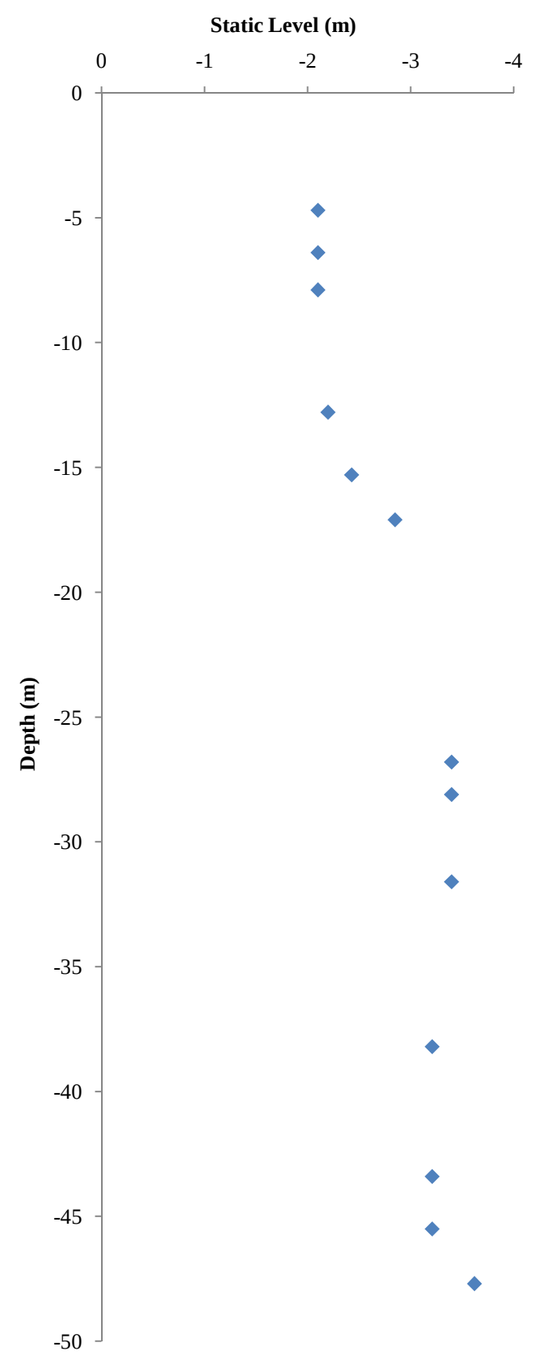


Figure 2.2c: Static water levels wit depth for O28w/0219

2.2.2 XRD Analysis

During the extension of well O28w/0219 samples were collected for XRD analysis of clast and matrix material. The aim of this is to identify the dominant minerals present in the valley gravels and identify whether these could account for the elevated salinity. The dominant material identified in the borelog of O28w/0219 is Torlesse derived sandstone, therefore, samples are expected to be high in quartz and feldspar. Appendix 2.1 contains XRD sample graphs.

A total of five samples were analysed to identify the crystalline material present. Samples A, B and C are samples of clasts, while samples D and E are of the matrix. Due to the drilling method it was very difficult to collect samples with significant clay content as most is washed away by the drilling fluids, for this reason only two samples were tested for clay composition. The clast samples are all Torlesse sandstone which accounts for almost all of the detrital material. Table 2.1 Contains the crystalline material present in samples A to E along with the depth from which the sample has been collected.

Table 2.1: XRD analysis results for 5 samples from well O28w/0219.

Sample	Sample Depth (m)	Quartz	Albite	Muscovite	Clay Minerals
		%	%	%	%
A	40.8	70	30	-	trace
B	48.2	65	35	trace	trace
C	20.6	50	40	-	10
D	26	75	25	-	trace (Kaolinite)
E	49.1	80	20	trace	trace (Kaolinite)

All samples analysed consisted almost entirely of quartz and albite. Muscovite is present in samples B and E in trace amounts. Clay is present in all samples at trace levels except in sample C, which contains 10% clay. Matrix samples have a higher percentage of quartz compared to the clast samples, reflecting the higher resistance of quartz to weathering compared to albite. Kaolinite is the only clay identified in the two samples tested for clay composition, however, it is only present in trace amounts. Kaolinite is derived from the decomposition of feldspars, a significant component of Torlesse sandstone, therefore, it is expected that kaolinite is the dominant type of clay in the valley.

2.2.3 Aquifer Delineation

Identifying the hydraulic properties of the subsurface is critical to understanding the nature of the groundwater. Aquifer tests are an important tool for assessing hydraulic properties including the hydraulic conductivity, transmissivity, and storativity. Aquifer testing consists of a well pumped for a designated time frame at a constant rate while drawdown is measured in the pumped well and at least one observation well. Two pump tests of significant importance to this study have been completed within the study area prior to this investigation. The pumping wells for each test are situated very close to the multi electrode resistivity survey lines, carried out during this study. The parameters defined by the aquifer tests will have a direct relevance to the interpretation of the resistivity profiles. Figure 2.1 shows the locations of the wells relevant to the two pump tests.

2.2.3.1 Speargrass Formation Pump Test

A 24 hour pump test was completed on O28w/0226 well from the 26th to the 27th of April 2007 by Butt Drilling Ltd. Three observation wells were used in this aquifer test including O28w/0122, O28w/0191, and O28w/0027. Figure 2.3 and 2.4 show the time versus drawdown for the pumped well and the three observation wells respectively. Appendix 2.2 contains borelogs of the observation wells.

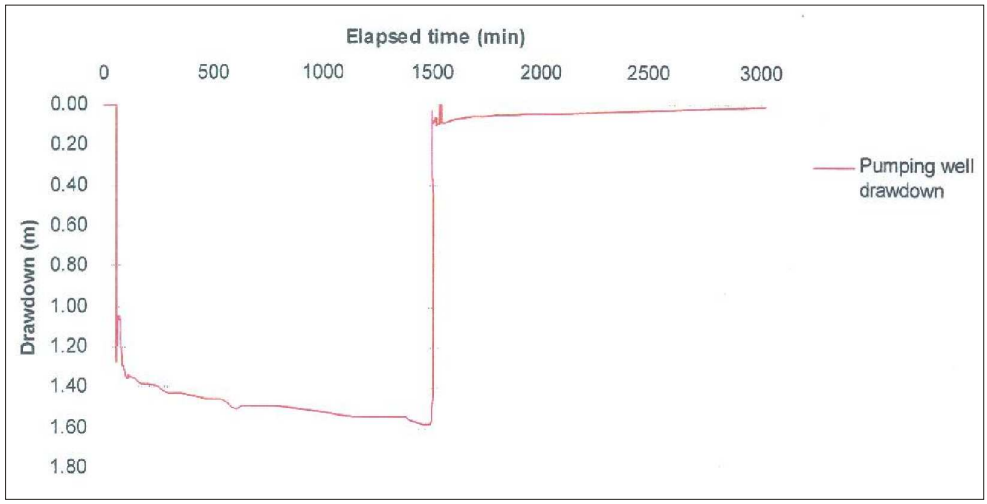


Figure 2.3: Drawdown versus time for pumping well O28w/O226 (MWH, 2007).

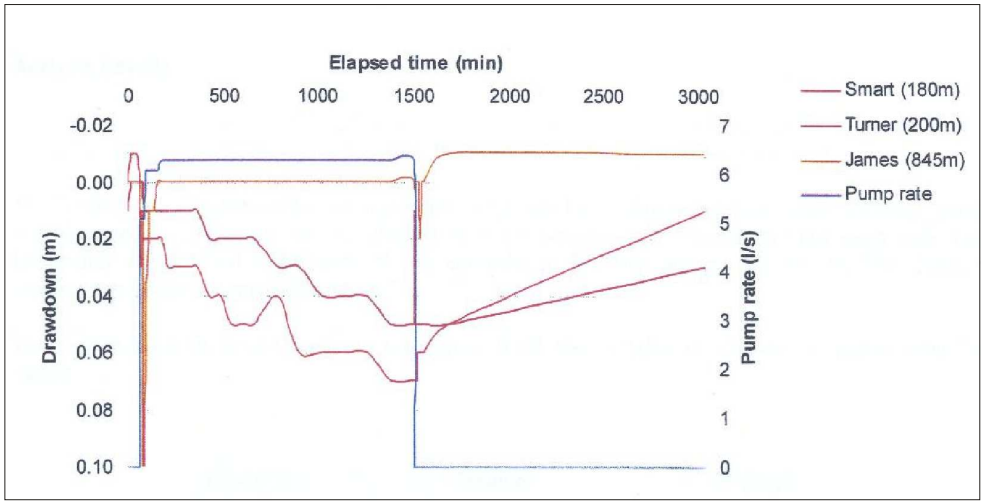


Figure 2.4: Drawdown versus time for the three observation wells relative to the pump rate (MWH, 2007).

Transmissivity values were calculated by MWH (2007) using four methods of analysis and are displayed in Table 2.2. The Cooper-Jacob Distance Drawdown method was considered to give best results due to the incorporation of data from three observation wells.

Table 2.2: Transmissivity and storativity data for the O28w/0226 pump test (MWH, 2007).

Data Source	Analysis Method	Transmisivity (m^2/day)	Storativity
Observation wells O28w/0191, O28w/0027, & O28w/0122	Cooper-Jacob Distance-Drawdown	1700	0.007
Observation well O28w/0191	Cooper-Jacob Steptest	1990	-
Observation well O28w/0027	Cooper-Jacob Steptest	1680	0.01
Observation well O28w/0191	Theis Steptest	1270	-

2.2.3.2 Reworked Speargrass Formation Pump Test

The aim of the aquifer test at O28w/0220 was to define the hydraulic properties of the Wairau Valley Aquifer at Mill Road and to determine the relationship between Mill Stream and the Wairau Valley Aquifer. On the 12th and 13th of December 2006 a pump test conducted at O28w/0220 by the Marlborough District Council. O28w/0219 was used as the observation well. Both the north and south branches of Mill Stream were monitored during pumping. At the time of the pump test, O28w/0219 extended to a depth of 15 m. Pumping well O28w/0220 extends to 12 m into reworked river gravels with a slotted PVC screen between 10-12 m. Pumping of the well was completed over a 47 hour period. Figure 2.5 shows the drawdown data for the pumping well. Initial drawdown is rapid and represents release of water from storage in a confined

aquifer. The levelling out of drawdown is attributed to delayed yield as the natural aquifer conditions and the drawdown cone reach equilibrium. After the first hour the rate of drawdown stabilises, therefore, recharge is approximately equal to the pumping rate (MDC Groundwater Group, 2007).

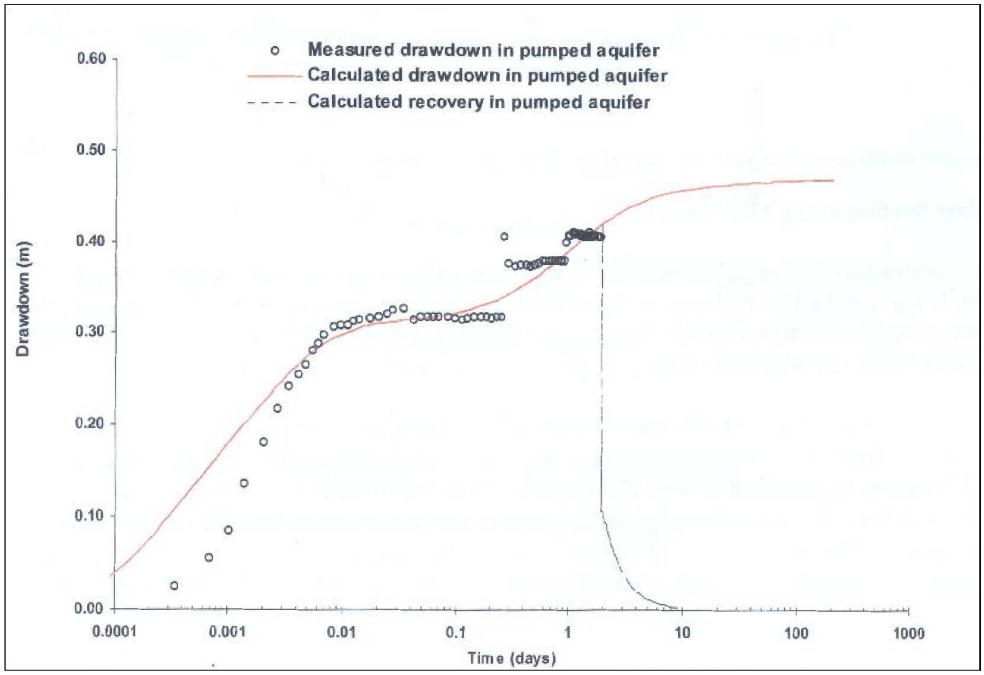


Figure 2.5: Measured drawdown of pumping well O28w/0220 compared to the calculated drawdown and recovery of the pumped aquifer for the given boundary conditions (MDC Groundwater Group, 2007).

Figure 2.6a shows the drawdown versus time for the pumping well and the observation well, Figure 2.6b shows the observation well in more detail. Two rapid increases in the drawdown occur at approximately 300 minutes and one day, respectively, with drawdown again stabilising after each event. The increase in drawdown is attributed the cone of depression reaching the southern edge of the Wairau Valley Aquifer, which is defined by the large degradation terrace approximately 375 m south of O28/0220. The second event is thought to be the result of a similar situation, possibly from a water bearing layer pinching out (MDC Groundwater Group, 2007).

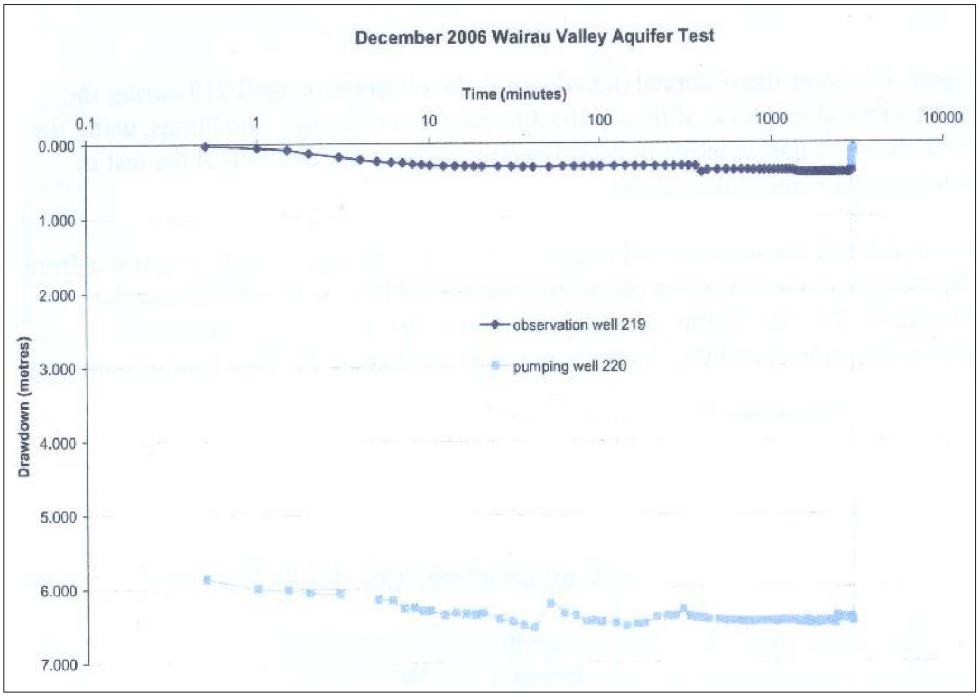


Figure 2.6a: Drawdown versus time for pumping well O28w/220 and observation well O28w/0219 (MDC Groundwater Group, 2007).

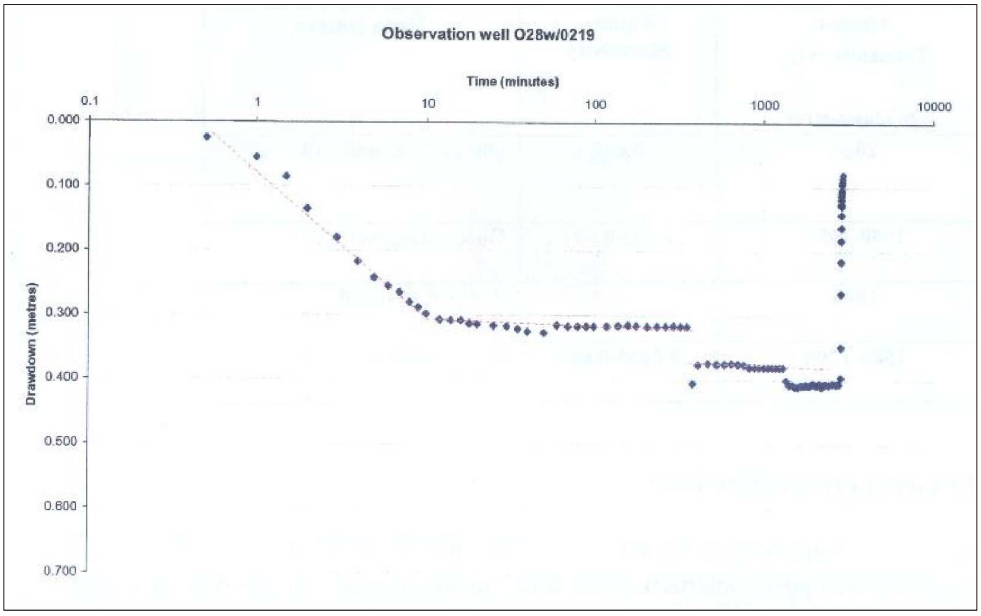


Figure 2.6b: Drawdown/Recovery versus time for the observation well O28w/0219 (MDC Groundwater Group, 2007).

Where drawdown is stable, water from both Mill Stream channels is probably recharging the aquifer at the rate the water is being pumped from the well (MDC Groundwater Group 2007).

The aquifer transmissivity was calculated by MDC at 1030 m^2/day to 2000 m^2/day using several different analysis methods (Table 2.3).

Table 2.3: Transmissivity and storativity data for the Salvador pump test at O28w/0220 (MDC Groundwater Group 2007).

Data Source	Analysis Method	Transmisivity (m^2/day)	Storativity
observation well O28w/0219	Hunt stream depletion equation type curve fitting	2000	0.002
observation well O28w/0219	Theis type curve fitting	1050 - 1987	0.002 - 0.007
Pumped well O28w/0220	Cooper-Jacob line of best fit	1030	-
observation well O28w/0219	Cooper-Jacob line of best fit	1590 - 1799	0.0035 - 0.005

2.3 Southern Hills Recharge and Surface Water

Using Stable Isotope Analysis Taylor (2003) identified Southern Hills runoff as the recharge source of the Wairau Valley Aquifer and showed that the Wairau River appeared to have little control on the south bank groundwater system. Speargrass Gravels fill the Wairau Valley and have been identified as relatively tight and generally poor water bearing. It is not well understood how the Southern Hills recharge transfers across the Wairau Fault and the major terrace riser defining the edge of the Wairau Valley Aquifer. Water loss from Mill Stream, as it meanders across the lower valley surface, has been identified by work completed by the Marlborough District Council. However, this cannot account for all of the recharge in the Wairau Valley Aquifer at Mill Road.

Within the study area are three streams which could potentially recharge the Wairau Valley Aquifer around Mill Road. These include Boundary Creek, Huddleston Stream, and Excell Stream (Figure 2.7). Spring locations and the subsurface flow path of Boundary Creek recharged groundwater are thought to be important to the problem. Walkers and Hillersden Streams also enter the Wairau Valley within the study area. However, due to their flow path they are not significant with respect to the Wairau Valley Aquifer at Mill Road. Boundary Creek is the most significant source of recharge from the Southern Hills. Huddleston Stream and Excell Stream contribute significantly smaller quantities due to smaller catchment sizes (Table 2.4). Boundary Creek, Excell Stream, and Huddleston Stream have perennial surface flow within the Southern Hills. Upon reaching the valley floor almost all stream flow contributes to groundwater recharge. The Boundary Creek reach from the Southern Hills to the Wairau River is a losing stream and

surface flow is only present during the winter months. Excell and Huddleston streams have losing reaches from the Southern Hills to immediately south of the Wairau Fault where springs recharge the streams. Downstream from the springs both Excell and Huddleston streams contain perennial surface flow. Excell and Huddleston streams recharge Mill Stream on the Holocene degradation surface (Wr 1).

Table 2.4: Catchment sizes for selected Southern Hills streams.

Tributary	Catchment Area Km^2	Elevation of the lowest point in the Catchment (m ASL)	Elevation of the highest point in the Catchment (m ASL)
Boundary Creek	39.8	240	1360
Excell Stream	9.7	220	1038
Huddleston Stream	6.9	220	1038
Walkers Stream	16.3	220	900
Hillersden Stream	29.7	190	944

A stream gauging survey was completed on the 31st of August 2007 to determine the surface water loss across either side of the Wairau Fault and in Mill Stream on the lower terrace. Stream Gauging locations are shown in Figure 2.7; data is shown in Table 2.5. Site 1 measured the flow rate in Boundary Creek before it has reached the valley floor and surface flow is lost to the groundwater system. This gauging reflects the surface water contribution of Boundary Creek to the valley. The gauging at Site 1 recorded a flow rate of 184 l/s. Sites 2 and 3 measure the Excell and Hillersden streams respectively. The sites are located approximately 500 m downstream from the springs that recharge the streams. On the day of the survey the reach of both Excell and Huddleston between the Southern Hills and the Wairau Fault contained no flow. Therefore, the gauging completed on each stream is entirely sourced from the springs located close to the fault trace (Figure 2.8). Excell Stream had the highest flow rate of 106 l/s compared to 78 l/s for Huddleston Stream. The sum of site two and three is 184 l/s, which is equal to the Boundary Creek measurement, however, this does not necessarily reflect a simple groundwater connection. Site 4 measured the flow rate in Excell Stream 2 km downstream from Site 2. Approximately 400 m upstream from Site 4 a tributary from Huddleston Stream flows into Excell Stream, this is reflected in higher flow rates of 144 l/s and 149 l/s measured. Two gaugings were completed at Site 4 because gusty wind conditions made it more difficult to keep the flow meter stable while collecting the data. However, the two measurements are relatively close and are considered reliable. The flow rate measured at Site 4, for Huddleston Stream dropped to 35 l/s, close to half the flow rate measured 1.2 km upstream (Site 3). The sum of Huddleston and Excell Streams at

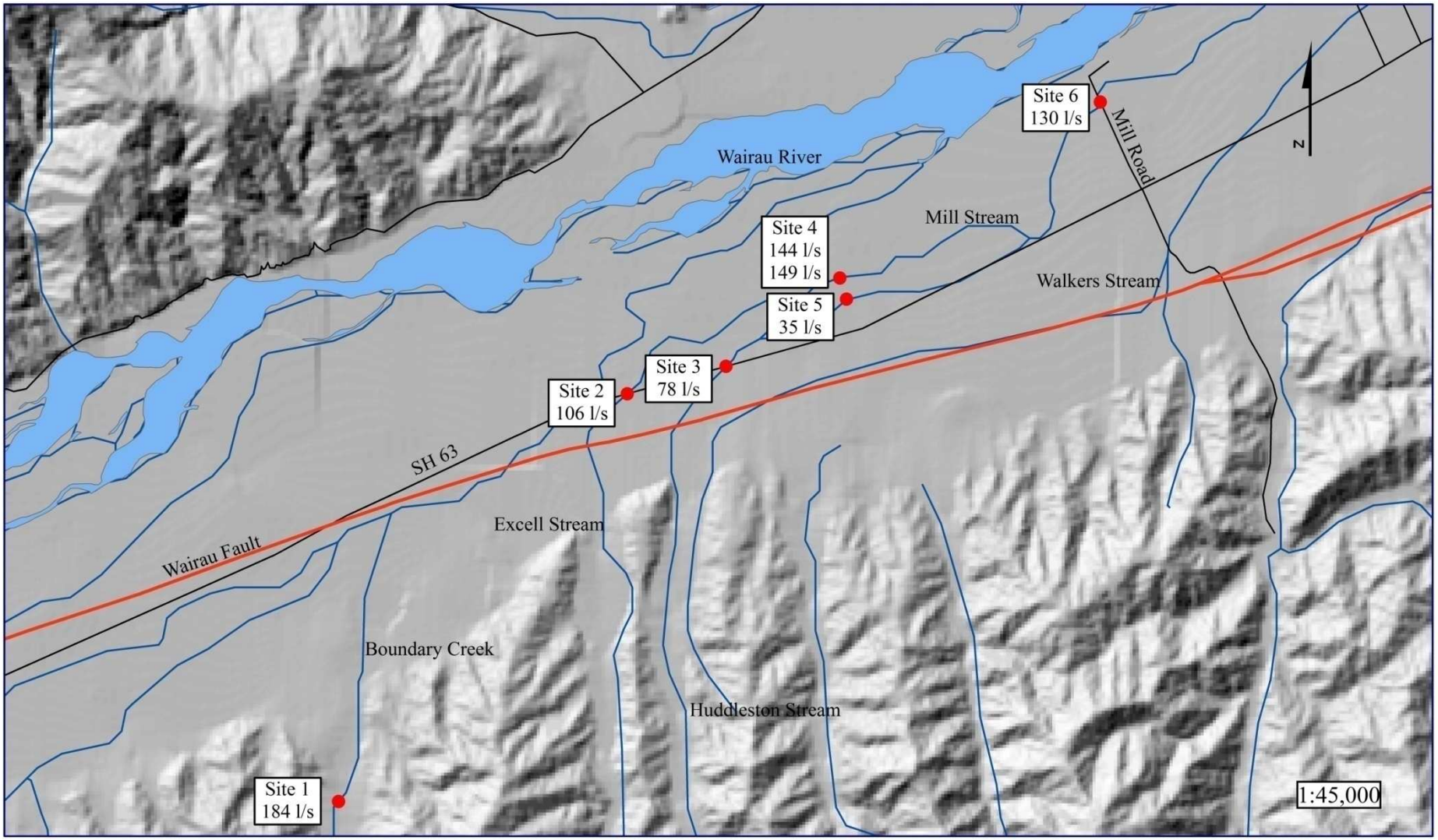


Figure 2.7: Map of the stream gauging sites and the flow rate measured.

Sites 4 and 5 give a total of 179 l/s and 184 l/s which is almost identical to the upstream flow rates. Site 6 is located at the Mill Stream ford at Mill Road, the flow rate measured here was 130 l/s. This represents a reduction in the flow rate by approximately 50 l/s from the combined flow of Sites 4 and 5 located approximately 3 km upstream.

Table 2.5: Gauging measurements for the south bank survey completed on the 31st of August 2007.

Site Number	Stream	Easting	Northing	Flow Rate l/s	Summed Flow Rate l/s
Site 1	Boundary Creek	2545319	5953891	184	184
Site 2	Excell Stream	2547656	5957199	106	184
Site 3	Huddleston Stream	2548456	5957421	78	
Site 4	Excell Stream	2549378	5958138	144 and 149	179 and 184
Site 5	Huddleston Stream	2549432	5957966	35	
Site 6	Mill Stream	2551487	5959567	130	130

This low gauging survey accounts for Southern Hills recharge derived from Boundary Creek, however, it does not account for Excell and Huddleston stream inputs. Furthermore, it is expected that there is some groundwater flow west of Boundary Creek between the Southern Hills and the Wairau Fault.

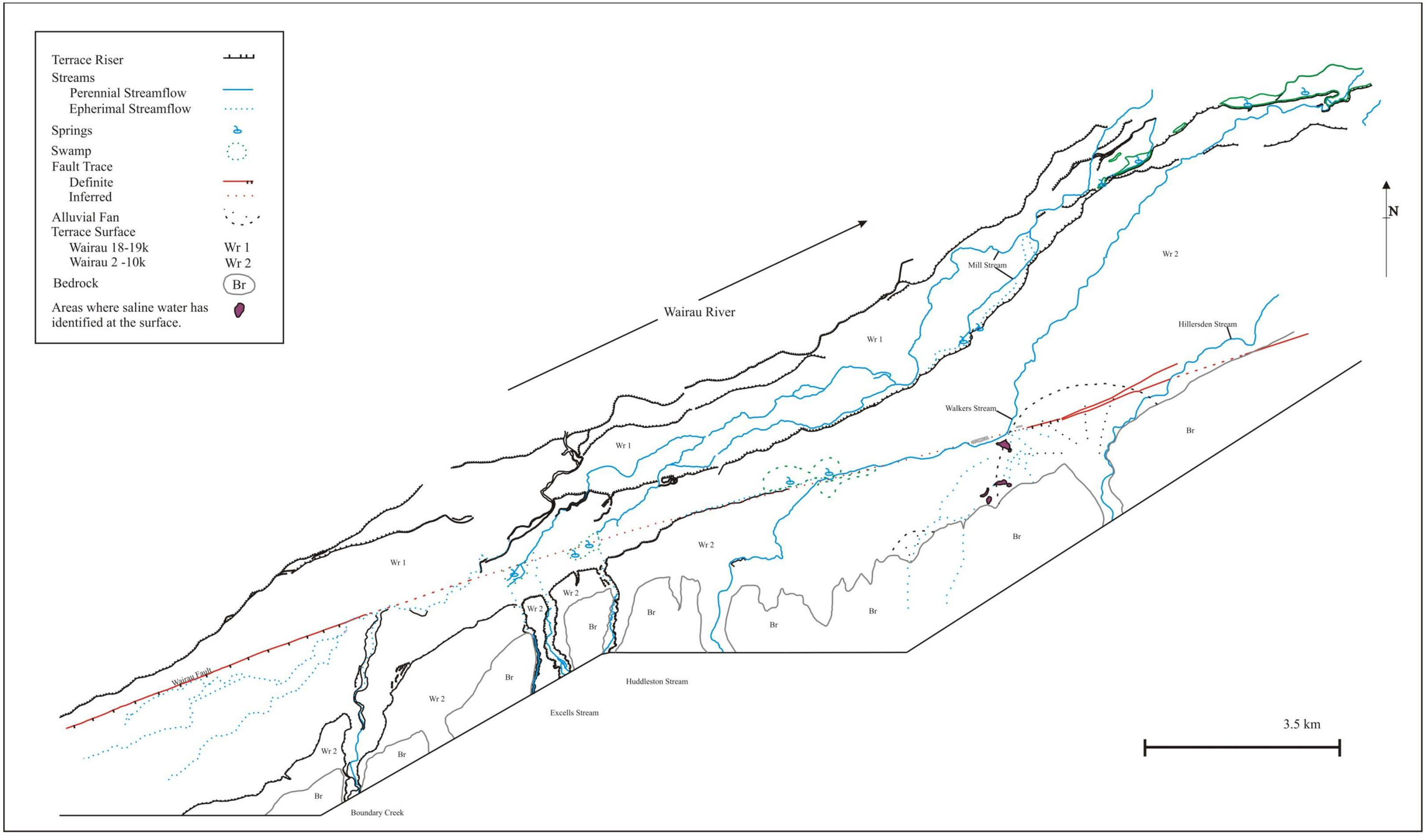


Figure 2.8: Aerial trace of the south bank showing the stream flow pattern

North of the fault trace Excell and Huddleston streams show no loss of surface flow to the groundwater system. On the Holocene surface the reach between Sites 4 and 5 to Site 6 represents a losing reach of approximately 50 l/s. Within this reach is a significant meander in the channel, approximately 400 m east, several springs emerge at the base of the terrace riser (Figure 2.8). These springs which recharge the southern strand of Mill stream would account for this loss from the main Mill Stream channel, however, a gauging was not possible at the time due to time constraints. Similar variations in the flow rate in Mill Stream had been recorded by previous Marlborough District Council gauging (V. Wardsworth, pers. comm., 2007).

2.4 Chapter Summary

The Speargrass gravels which fill the Wairau Valley have a lower permeability compared to the thin layer (approximately 15-20 m) of reworked Speargrass gravels below the Wr 1 terrace surface which defines the Wairau Valley Aquifer. Conductivity at well O28w/0219 increases sharply at approximately 17 m and show some variation to 25 m where conductivity is consistently greater than 5,000 mS/m. Static water levels measured at varying depths during extension of well O28w/0219 suggest gravity drainage is occurring in the valley, however, due to the nature of fluvial deposits natural variations may occur. The composition of clasts is almost entirely Torlesse sandstone. Quartz and Albite are the dominant minerals with minor mica identified in the XRD analysis. Kaolinite is the only clay identified in the samples analysed, probably as result of the weathering of feldspars. A surface water deficit is identified across the fault. Analysis of stream flow gauging of the south bank streams shows some water loss from the southern hills across the Wairau Fault which must be traversing the fault as groundwater.

CHAPTER THREE

SUBSURFACE GEOPHYSICAL INVESTIGATIONS

3.1 Introduction

The aim of this chapter is to introduce Multi-Electrode electrical Resistivity (MER) data collected in the Wairau Valley for this study. The objectives of the geophysical investigations are stated along with the theory behind the methods used.

The main objective of the MER surveys is to better define the spatial extent of the subsurface, saline water along Mill and Parsons Road. Knowledge of the distribution of the salinity is important when considering groundwater allocation.

Electrical properties of the subsurface are largely controlled by pore fluid, moisture content, soil type (i.e. clay) and metal content (Loke, 2004). Of these, where metals are not present pore fluid will dominate the response therefore resistivity profiling is a technique commonly applied in groundwater investigations, especially where moderate to high salinities are present (Nobes, 1997a).

Below Mill Road, total dissolved solids concentrations reach 31,000 mg/L at depth, concentration of saline groundwater in the subsurface is considered the major controlling factor in the electrical properties of the subsurface. The MER method was chosen because it would give a continuous longitudinal profile of the subsurface instead of point locations of the time-domain electro-magnetic, it is relatively simple to use for both data collection and processing, and only a small field crew is required. Weather is not a major factor for MER as it is with other types of geophysical methods, rain tends to improve ground contact. The time required to acquire data for a single line is generally the most significant factor in collecting all data in a specific time frame. Prior to this study no shallow geophysical surveys had been completed in the field area.

3.2 Basic Principles of MER

3.2.1 Resistivity Theory

The MER technique generates a 2D pseudo-section using an array of four electrodes, two voltage and two current electrodes to delineate the subsurface resistivity distribution. Artificially induced current is added to the ground and the potential change is measured at the surface, giving the apparent resistivity of the subsurface geology (Kearey and Brooks, 1991).

The resistivity (ρ) of a material is defined as the resistance between opposing sides of a cube (Kearey and Brooks, 1991), it is an intrinsic property of any material. The electrical resistance (R) of a material is defined as the impedance of electron movement during current flow (Gibson & George, 2003). Resistance is directly controlled by the length (L) of the flow path and the cross-sectional area (A). The resistance and resistivity are directly related to each other by the equation below (unit = ohm meters, Ω m):

$$\rho = \frac{RA}{L} \qquad [3.1]$$

The reciprocal of this is termed conductivity σ (unit = Siemens).

$$\rho = \frac{1}{\sigma} \qquad [3.2]$$

In a medium of uniform resistivity the current injected into the ground will flow radially from the input source in all directions (Figure 3.1) and the voltage potential at a point will vary inversely with distance from the current source.

$$V_{(r)} = \rho \frac{I}{2\pi r} \qquad [3.3]$$

Where, $V_{(r)}$ = voltage potential at a given distance (r) from the current electrode

I = current input (Amps)

ρ = resistivity of the medium

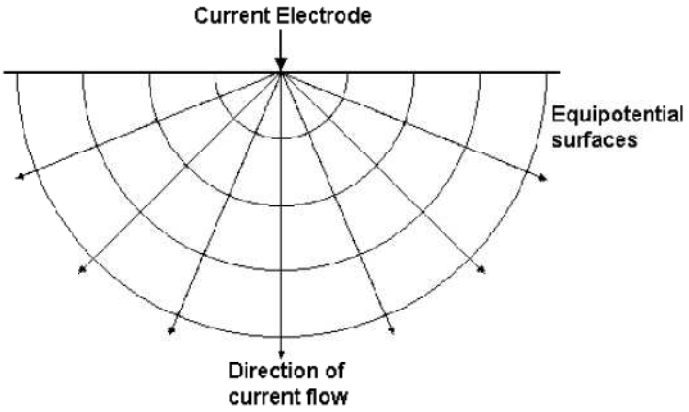


Figure 3.1: Current flow from a point source in a homogenous medium (Kearey and Brooks, 1991).

Because MER surveys use two current (source and sink) electrodes the potential of any point is given by:

$$V_{(r)} = \rho \frac{I}{2\pi r_1} - \rho \frac{I}{2\pi r_2} \qquad [3.4]$$

Where, r_1 and r_2 are the distances from the two current electrodes

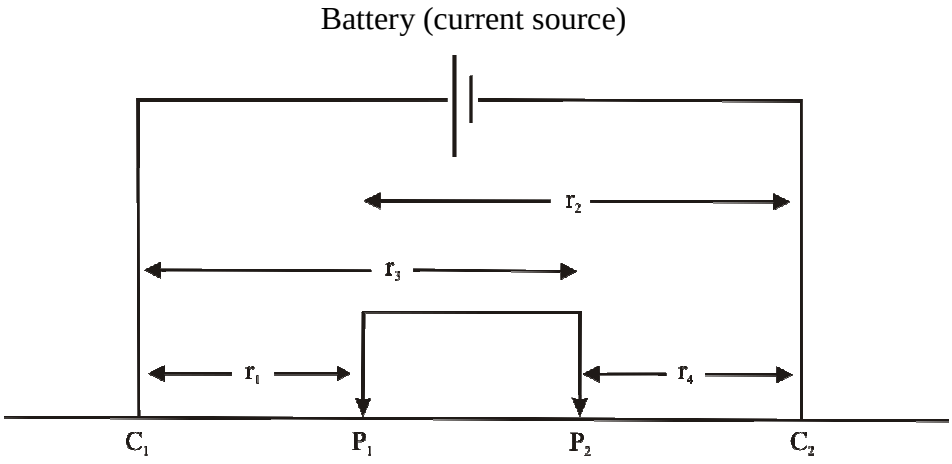


Figure 3.2: Generalised configuration of electrodes used in electrical resistivity surveying. C_1, C_2 = current electrodes, P_1, P_2 = potential electrodes (Gibson & George, 2003).

Since we are measuring the potential difference across a known distance (Figure 3.2) two potential electrodes set up between the two current electrodes measure the potential difference ΔV between them, this is expressed as:

$$\rho = \frac{2\pi r \Delta V}{I}\left(\frac{1}{\frac{1}{r_1}-\frac{1}{r_2}-\frac{1}{r_3}+\frac{1}{r_4}}\right) \qquad [3.5]$$

The resistivity of a homogenous medium can be calculated if the distances between each electrode are known, the current applied to the source electrode (C_1 in Figure 3.2), and the potential difference ΔV is measured.

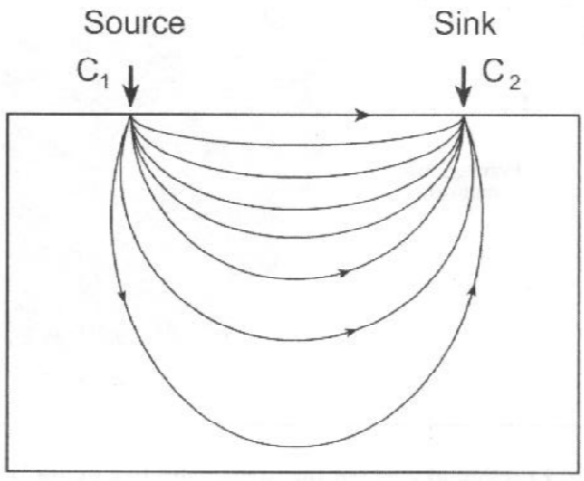


Figure 3.3: Flow between current electrodes (Gibson & George, 2003).

Current flow between the two current electrodes will flow through different pathways of varying depth (Figure 3.3). The percentage of flow is not equal for each current pathway. The equation below shows that the fraction of the total current (I_f) that penetrates to a depth (z) is related to the electrode spacing (a):

$$I_f = \frac{2}{\pi}\tan^{-1}\left(\frac{2z}{a}\right) \qquad [3.6]$$

The current distribution is dependent on the ratio between current depth and electrode spacing. 70% of the total current flow between the two electrodes will be at a depth less than the electrode

spacing, therefore, to reach greater depths in a single survey the electrode spacing must be increased. In a homogenous medium the resistivity will not change with depth so changes in electrode spacing will not produce changes in the resistivity values.

In practice, the subsurface is never homogenous. To determine the resistivity values for a layer at depth the electrode spacing must be increased. Where current flows through more than one layer equation 3.5 will give the apparent resistivity (ρ_a) which is re written below:

$$\rho_a = \frac{2\pi\Delta V}{I}\left(\frac{1}{\frac{1}{r_1}-\frac{1}{r_2}-\frac{1}{r_3}+\frac{1}{r_4}}\right) \qquad [3.7]$$

The apparent resistivity will lie in between the resistivity values for the two layers, it is not the average of the true resistivity of the two layers (Gibson & George, 2003).

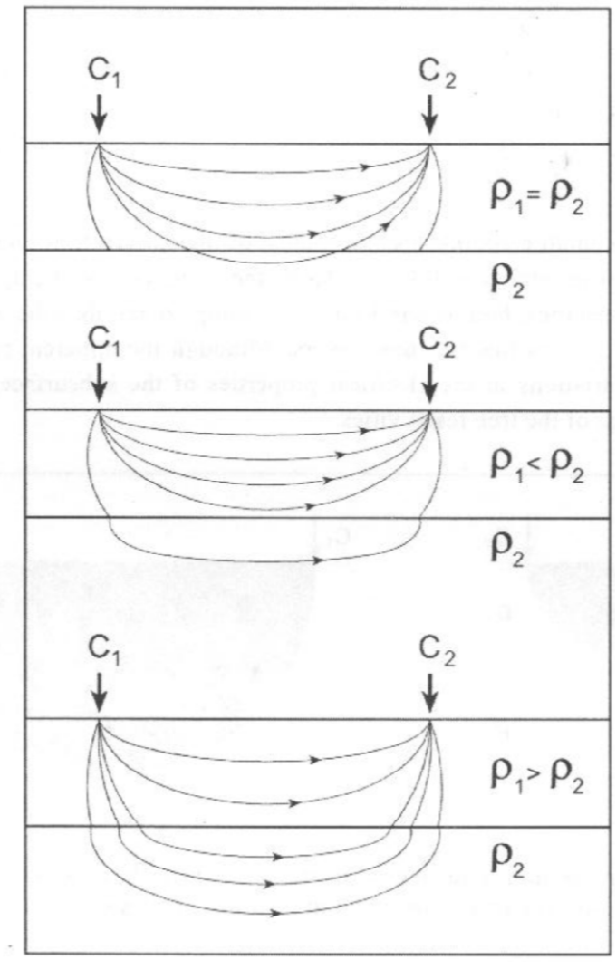


Figure 3.4: Schematic representation of current flow in the two layered model (Gibson & George, 2003).

Figure 3.4 shows the way current will preferentially flow through the layers of least resistivity. If the upper layer has a higher resistivity then the current will preferentially flow at depth. It is important to note that this is a very basic representation of non homogenous current flow. In practice, current flows in a three dimensional framework through layers of varying resistivities, with discontinuities such as faults and fractures common throughout the subsurface, forming a very complex distribution of the resistivity of the subsurface.

3.2.2 Array Configuration

There are a variety of electrode arrays for resistivity surveys, all have advantages and disadvantages depending on the aim of the electrical survey. Many authors have discussed these for each survey type (Kearey and Brooks, 1991; Reynolds, 1997; Gibson & George, 2003; Milsom, 2003). Accordingly only the Wenner array will be discussed here, as this was used in this study.

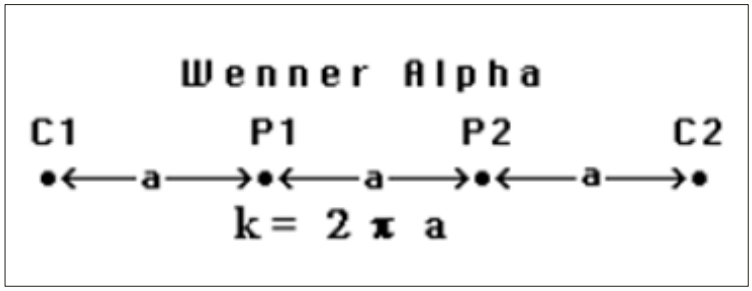


Figure 3.5: Wenner array configuration, C_1 is the source electrode, C_2 is the sink electrode, P_1 and P_2 are the potential electrodes (Loke, 2004).

The Wenner array (Figure 3.5) consists of four electrodes, two potential electrodes in between two current electrodes. Spacing is constant as it is moved across the survey line. At each new passing the electrode spacing is increased to gather data at depth (Figure 3.6). As the electrode spacing is increased fewer data measurements can be collected, therefore, the number of readings decreases with depth. The collection of these data points creates a 2D profile of the subsurface along the survey line.

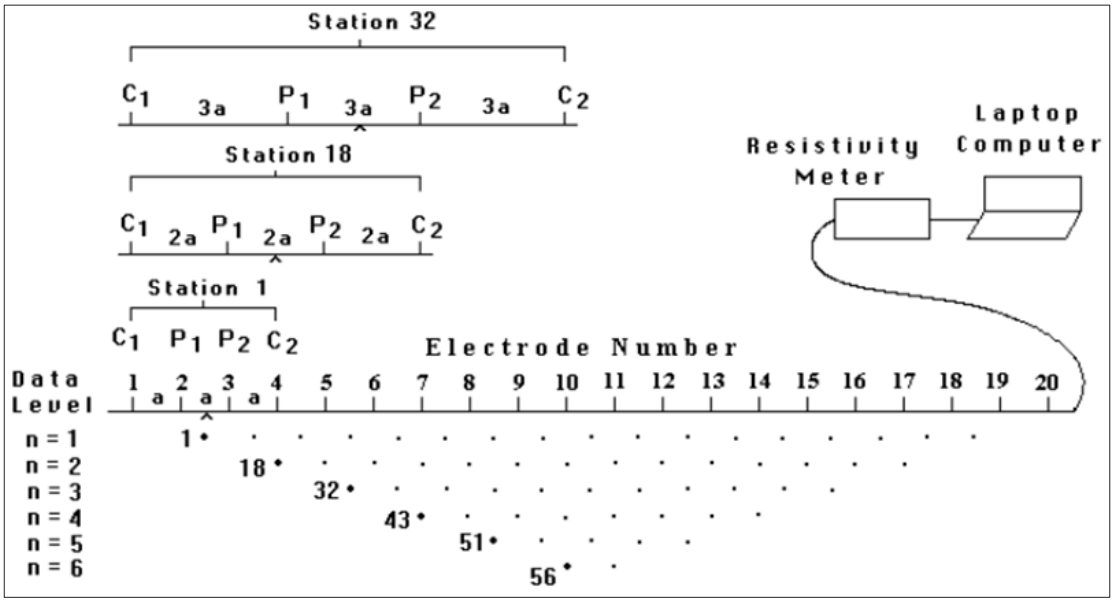


Figure 3.6: The arrangement of electrodes for a 2-D electrical survey and the sequence of measurements used to build up a pseudo-section using the Wenner electrode array (Loke, 2004).

Equation 3.7 can be rewritten to include the known geometric factor K:

$$\rho_a = K \frac{\Delta V}{I} \qquad [3.8]$$

K varies depending on the electrode array geometry, the Wenner array is calculated using:

$$K = 2\pi \left(\frac{1}{\frac{1}{r_2} - \frac{1}{r_2} - \frac{1}{r_4} + \frac{1}{r_4}} \right) \qquad [3.9]$$

This can be reduced down to:

$$\rho_a = 2\pi a \frac{\Delta V}{I} \qquad [3.10]$$

The Wenner array has several advantages and disadvantages which must be taken into account when designing a survey. The signal strength is higher in the Wenner array compared to the other common arrays such as the Schlumberger, Pole-Dipole and Dipole-Dipole. This is important where high background noise is present. Sensitivity for a specific configuration provides information on the influence of subsurface resistivity variations on the potential by the

array. For the Wenner array the 2D sensitivity contours are horizontal so it is much better at detecting vertical changes than lateral changes. As a result it is best suited to unfolded sedimentary terrain. The Dipole-Dipole method is best at delineating horizontal resistivity variations, e.g. igneous dikes, because its sensitivity contours run approximately vertical. For a given survey length, the Schlumberger configuration will be able to collect data at greater depths compared to the Wenner array due to the differences in electrode separation on each passing of a survey line, allowing more data points to be collected (Loke, 2004).

3.2.3 Depth of Penetration

The depth of penetration for a particular survey is dependent on two factors, the electrode separation and the subsurface resistivity layering (Lapwood, 2007), therefore, we are unable to determine the depth of penetration prior to starting the survey as the subsurface resistivity layering is what we wish to determine. The median depth of investigation using the Wenner array is approximately half the electrode spacing (Gibson & George, 2003). The detection of deep resistivity interfaces is affected by the resistivity contrast at the interface and the amount of background electrical noise (Milsom, 2003).

3.2.4 Electrical properties of the subsurface

Electrical properties of the subsurface are dependent on many parameters including the pore water, moisture content and the type of strata e.g. metal content in the underlying geology will dominate the electrical response, and clays have low resistive values compared to most common rock types.

Below is the empirical formula for the effective resistivity of a rock by Archie (1942):

$$\rho_e = \alpha \Phi^{-b} f^{-c} \rho_w \qquad [3.11]$$

Where ρ_e = effective resistivity,

Φ = porosity,

f = fraction of pores containing water,

ρ_w = resistivity of the pore water, and

α, b, and c are empirical constants

Pore fluid is arguably the most important control on a rocks ability to conduct, as most minerals are insulators (Kearey and Brooks, 1991). In general, as porosity increases, the resistivity decreases. The effective resistivity of the subsurface is controlled by the resistivity of a rock and its pore water.

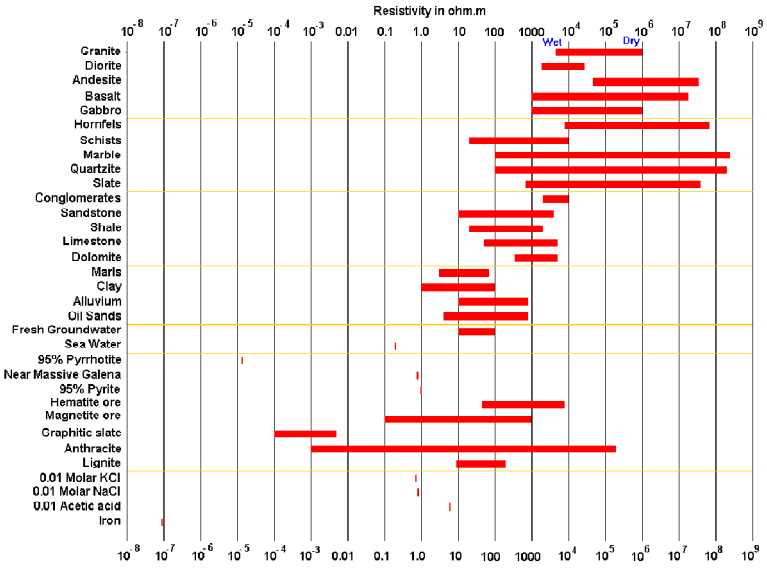


Figure 3.7: Resistivity of rocks, soils and minerals (Loke, 2004).

3.2.5 Equivalence

Equivalence is a term used to describe the problem of having a resistivity value that can be the result of many different geologic conditions. Only a distinct number of singular measurements can be measured with a limited number of electrodes, however, for an exact reconstruction of the resistivity distribution within the subsurface, the potential at every point on its surface must be known. Therefore, there are an infinite number of parameter distributions that cannot be distinguished by a finite set of measurements (Hoffmann and Dietrich, 2004). It is not possible in 2D software to include equivalent solutions because inversion follows a set optimization strategy, however, damping factors and flatness filters can be applied in the Res2dinv, v3.4 software used in this study (Gentomo, 2004).

3.2.6 Sensitivity and Uncertainty Profiles

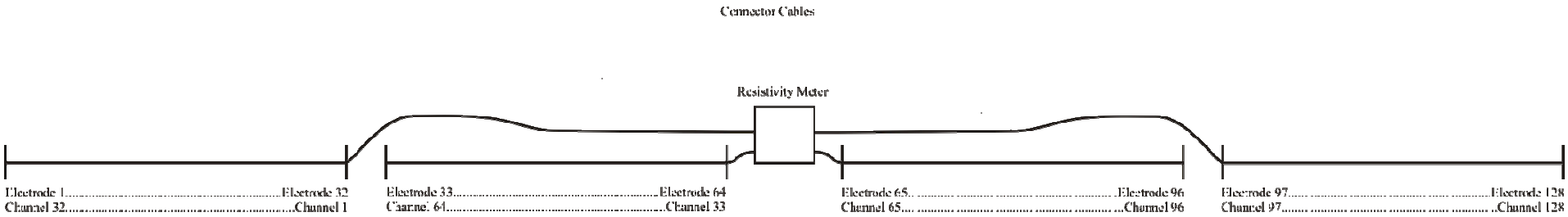
Sensitivity is a measure of quantity of information about the resistivity of a given cell within the dataset. Higher values give greater reliability of the model resistivity for that location, generated by the inversion process (Geotomo Software, 2004). Sensitivity will be highest close to electrodes and along the margins due to larger cell size at the sides and bottom of the profile.

Uncertainty is the root mean square (RMS) error per cell and is typically lower in the centre of the profile. Uncertainty values are useful only when variation in the subsurface resistivity is smooth, this is assumed by the smoothness constraint. Where uncertainty values are not useful, comparison between maximum and minimum resistivity profiles can help to determine the reliability of the dataset. Features present on both profiles are considered as reliable and a reflection of subsurface conditions (Loke, 2004).

3.3 Resistivity Surveying Methodology

3.3.1 System Components and Survey Set-up

The resistivity meter used in this study is the Geopulse Tigre 128 with ImagerPro 2000XL Version 1.0.0 software. ImagerPro is run on a laptop connected to the resistivity meter to control survey parameters. The ImagerPro 2000XL software is designed for Wenner 2D resistivity imaging array, with a maximum array of 128 electrodes. Electrodes are stainless steel probes approximately 30 cm in length. Electrodes are the contact between the ground and the cables, they need to be kept clean of corrosion around the clips which connect to the takeouts as this can create noise in the readings. Four take-out cables are used in this survey and two connector cables, each are multi-cored, individually wired to each electrode. The takeout cables consist of 32 takeouts at 5 m spacing along the length, each end of a takeout cable has the same plug. The connector cables are used as extensions to connect cables 1 and 4 to the Geopulse Tigre (Figure 3.8).



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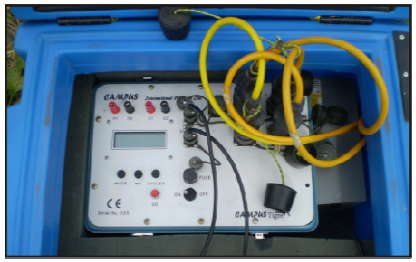

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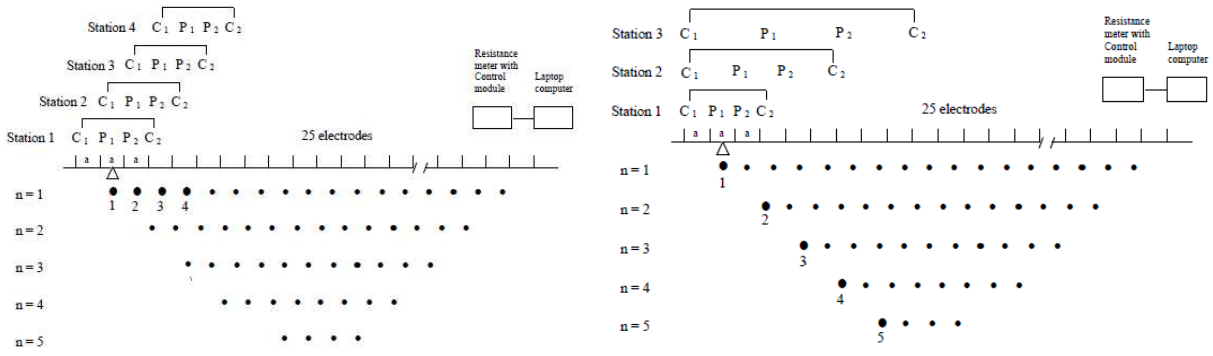
3

4

Figure 3.8. Channel and electrode layout. Picture 1, Campus resistivity metre; 2, Setting up survey line 1 along Mill Road; 3, Checking contact resistances for survey line three; 4, An electrode with good ground contact.

The four takeout cables are laid out along the survey line end to end. The electrode spacing used on all profiles is 5 m which is equal to the take-out spacing. Electrodes are inserted to a depth no more than 5% of the unit electrode spacing, an electrode is connected every take out except where ground conditions preclude electrode placement (e.g. takeout is positioned in the middle of a road). The Geopulse Tigre is set up between Cables 2 and 3, which connect directly to the resistivity meter. As stated earlier extension cables are used to connect the two end cables. Channel 32 (the last takeout on cable 1) represents electrode 1, the remainder are consecutively numbered up to electrode 128. Channels are numbered with the smallest number channel of each cable being the one closest to the center (Figure 3.8).

Both traverse and roll-on survey models are used in this study, each of which has a slightly different method of data collection. The traverse survey model is used where the total cable length available covers the entire profile distance. This method acquires all readings on a single layer before moving to the next (Figure 3.9a). Roll-on survey model (Figure 3.9b) is used where the survey line is greater than the total length of takeout cable available. In this survey there are four takeout cables for a total 128 electrodes and 640 m in length. Where the survey line is longer than 640 m measurements are collected at the first 32 data points of each layer and the data are saved, the first cable is then moved to the end of the line and process is repeated until the survey has reached the final cable position where the traverse model is used to complete the data collection.



a) Traverse model b) Roll-on model

Figure 3.9: The traverse and roll-on method of data collection used in this study (Loke, 2004).

3.3.2 Topography

Position of electrodes and elevation above sea level is collected using Trimble ProXR differential GPS which has an accuracy of 10 cm horizontal and 20 cm vertical. Because the Topographical data are exported from GPS Pathfinder software as a .dbf file, this can be viewed in Excel. The relevant data is copied into the associated resistivity data file and set out as described in Gentomo (2004).

3.3.3 Survey Design and Data Collection

3.3.3.1 Line 1

MER line 1 is located on the western edge of Mill Road beginning at the northern end approximately 150 m from the present location of the Wairau River running the entire length of Mill Road to State Highway 63 (Figure 3.10). The objectives of this survey line is to define the base of the Wairau Valley Aquifer, to define the extent of the saline water below Mill Road, to determine the influence of the Speargrass Terrace on the groundwater and determine the depth to basement if possible. Several wells close to line 1 give subsurface control, there locations are indicated in Figure 3.10. O28w/0219 is the deepest well in the field area at 50 m. It has been logged and groundwater conductivity measured with depth during drilling. O28w/0220 is a monitoring well in the Wairau Valley Aquifer with a depth of 12 m. This well has had a pump test carried out to determine Wairau Valley Aquifer properties. O28w/0027 gives the depth to water table on the upper terrace at the southern end of line 1. O28w/0124 is located on the lower terrace offset from line 1 approximately 250 m to the east and has a depth of 24.3 m. Line 1 consists of two surveys overlapping by one cable length or 32 electrodes. Survey 1A consists of 128 electrodes whereas 1B uses only 96 electrodes, the initial design was for two cable overlap but 1 cable failed to read any contact resistances in the field and had to be discarded from the survey, the problem was with one of the cable ends which had separated from some of the internal wires. As a result, the maximum depth of data acquisition for 1B is reduced, however, the total planned length of line 1 remains the same, only overlapping data were not collected. A total of 2667 data points were collected for survey 1A, and 1254 data points for 1B.

3.3.3.2 Line 2

MER line 2 is located on the upper terrace surface and runs parallel to Parsons Road offset approximately 250 m to the west (Figure 3.10). The line begins at State Highway 63 and runs to the edge of the Southern Hills. The objectives of this survey line is to understand how the saline

water moves from being at the near surface close to the Southern Hills to depths close to 20 m below the lower terrace and to identify the influence of the fault on subsurface groundwater flow. Ground control are inferred from well O28w/0219 on the lower terrace along with wells O28w/0226, a shallow well close to the start of line 2 which has been pump tested (refer to section 2.3.1.2). Line 2 consists of 2 surveys 2A and 2B, each consisting of 128 electrodes. Initially this line was to be a roll-on survey, however, cows were present on the land where 2B is located. This resulted in two field sessions being required to complete the line. Cows are excellent at damaging geophysical equipment, they particularly enjoy chewing on the cables after the initial fear of the unknown has passed (M. Finnemore, pers. comm., 2008), Survey 2A consists of 2667 data points collected, the maximum possible for a traverse survey model using 128 electrodes, Survey 2B was slightly less at 2368 data points due to time constraints in the field.

3.3.3.3 Line 3

Resistivity Line 3, the second line on the upper terrace runs parallel to Line 2, 750 m to the west (Figure 3.10). Line 3 was not in the initial survey design but after processing the line 2 pseudo-sections a significant gap became apparent between surveys 2A and 2B, this gap is in the area of the Wairau Fault trace. Furthermore several features visible in the line 2 pseudo-sections would improve there interpretation from a 3D perspective of the subsurface, so it was proposed to run a third line parallel to line 2 but 750 m further west. Line 3, unlike the previous two uses a roll-on model for data collection ensuring there are no sections along the line without data collected. It consists of 7 cables and 224 electrodes for a total length of 1120 m. The depth of penetration is lower for roll-on surveys than a single traverse because the maximum electrode separation is only 96 electrodes when the first cable must be rolled to the end of the line. Line 3 initially was designed for a total of 8 cables, due to time constraints this was not possible. It was planned to move further into the Southern Hills giving greater control on the bedrock profile of the valley. A total of 5584 data points were collected for line 3.

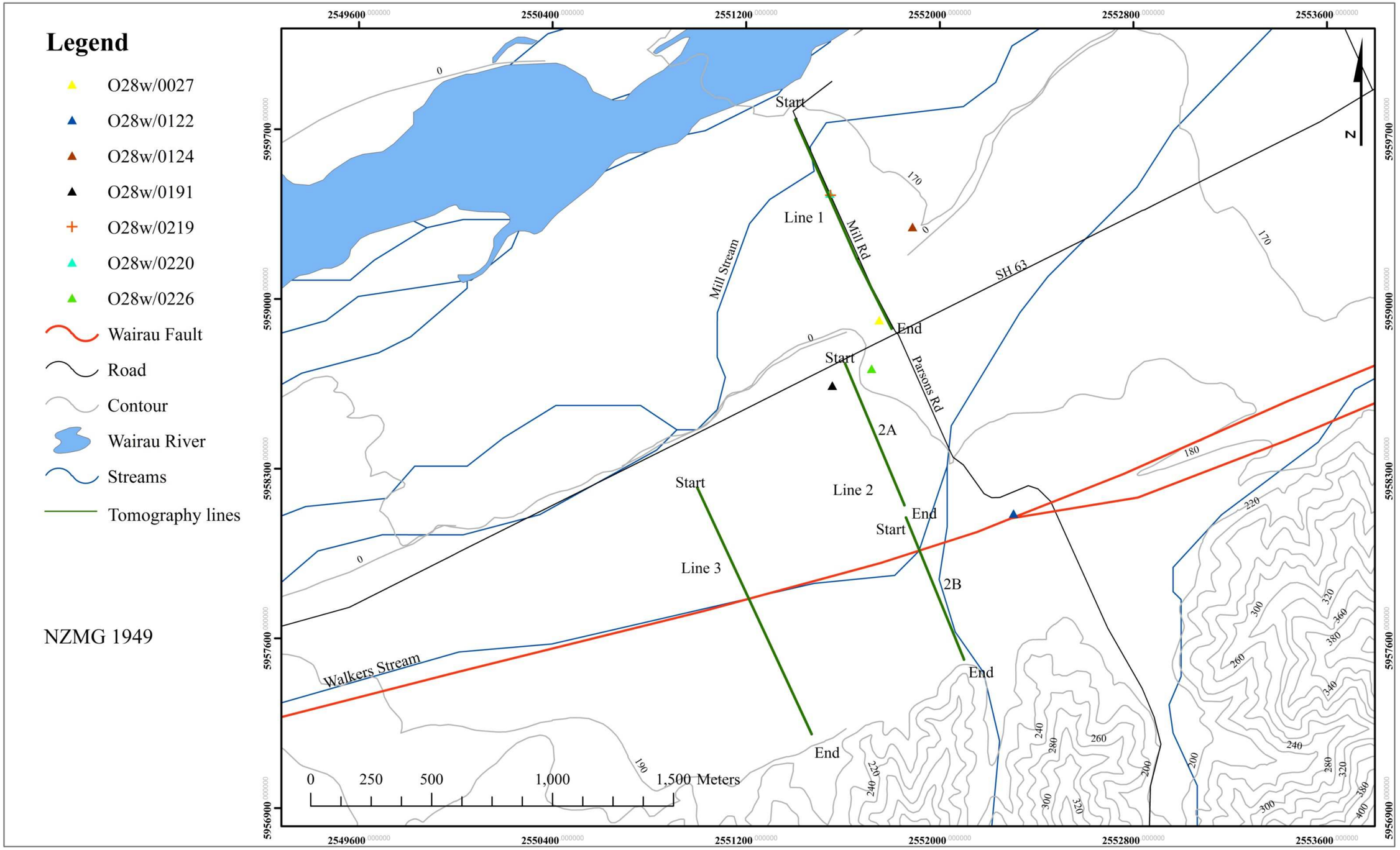


Figure 3.10: MER Survey Lines in the Wairau Valley.

3.3.4 Data Processing

3.3.4.1 Data processing Methods

The data collected are apparent resistivity values of the subsurface. Inversion of the raw data is required to develop an approximation of the actual subsurface resistivity. Data inversion generates a model that agrees with the measured values under given mathematical restrictions (Loke, 2004). Basic inverse theory from Loke (2004) can be found in Appendix 3.1.

Processing of the raw data is carried out using Res2dinv. Before this program can read the data files, they must first be converted from the .res file type of the ImagerPro software into a .dat file. This is done in the ImagerPro software by concatenating the files. This also combines roll-on files into a single dataset for inversion.

Once converted into .dat format the largest and smallest values can be removed by opening the dataset as a text file and simply delete the error values. This is useful where very low or high values are present that preclude the data being up loaded in the 'exterminate bad data points' window in the Res2dinv software. For the datasets in this study all data points with values (Ω m) equal to 0.0 are deleted and the largest values in the files are progressively removed until the dataset can be drawn in the 'exterminate bad data points' window.

The Gauss-Newton smoothness constrained least-squares (l_2) inversion method is used in this study. Smoothness constraint inversion is effective where the variations in subsurface occur in a gradual manner. The Gauss-Newton method gives the most accurate results when the survey displays large resistivity contrasts (Nguyen et al, 2005). The l_2 method aims to minimize the sum of the squared differences between the apparent and modeled resistivities (Kilner et al, 2005). It alters the model block through an iterative process until the Root Mean Square (RMS) error changes by less than 0.5% between iterations (Loke, 2004). After initial inversions of the dataset graphing the RMS error distribution shows the number of data points for each error value. This error represents the difference between the measured and model resistivity values, the highest bars should represent the lowest error values and exponentially decrease as error increases. RES2DINV allows the user to truncate the data higher than at the desired error or replace the values with the model resistivity values. In this study all data points above 100% apparent resistivity error were removed. Data related to the inverted profiles

displayed in this chapter including all raw data and inverted files are contained in Appendix 3.2. For each survey profile several pseudo-sections were created to determine the accuracy of the model, this includes unedited measured apparent resistivity data, measured apparent resistivity and calculated apparent resistivity after removal of bad data, model sensitivity and uncertainty, minimum and maximum resistivity pseudo-sections, RMS error distribution graph and the model resistivity pseudo-section with topography.

In all surveys (with the exception of line 3) a model electrode spacing of half of the actual electrode spacing is used due to the variation in near-surface apparent resistivity values. Halving the cell size has the effect of reducing the maximum possible misfit of the data (Loke, 2004). Each survey line is discussed individually with respect to factors affecting the data inversion.

3.3.4.2 Survey 1A

The measured apparent resistivity data for profile 1A (Figure 3.11) is significantly affected by bad data points in the measured apparent resistivity pseudo-section. All data at depth with an apparent resistivity greater than approximately 500 Ω m are considered bad data. This is because these data points show a clear symmetry with other anomalous data points that could only result from a bad electrode. A similar pattern of error did not occur in subsequent surveys suggesting that the problem is likely from the contact between the ground and the electrode or the takeout and the electrode. The most likely reason is poor contact to the ground as the equipment was checked and cleaned prior to entering the field. It was noted while placing the electrodes along line 1 that the soil horizon is often much less than 5 cm before hitting coarse river gravels. If the electrodes are wedged between gravel clasts which have a very high resistivity then this has a significant effect on that electrodes measured data. Figure 3.10 shows the pseudo-sections for survey 1A. Attempting to reduce the influence of bad data, 1017 data points were removed. This is a significant portion of the data set but gave the lowest error values. It does, however, limit the detail of interpretation for this survey and only largest scale feature can be interpreted with any certainty.

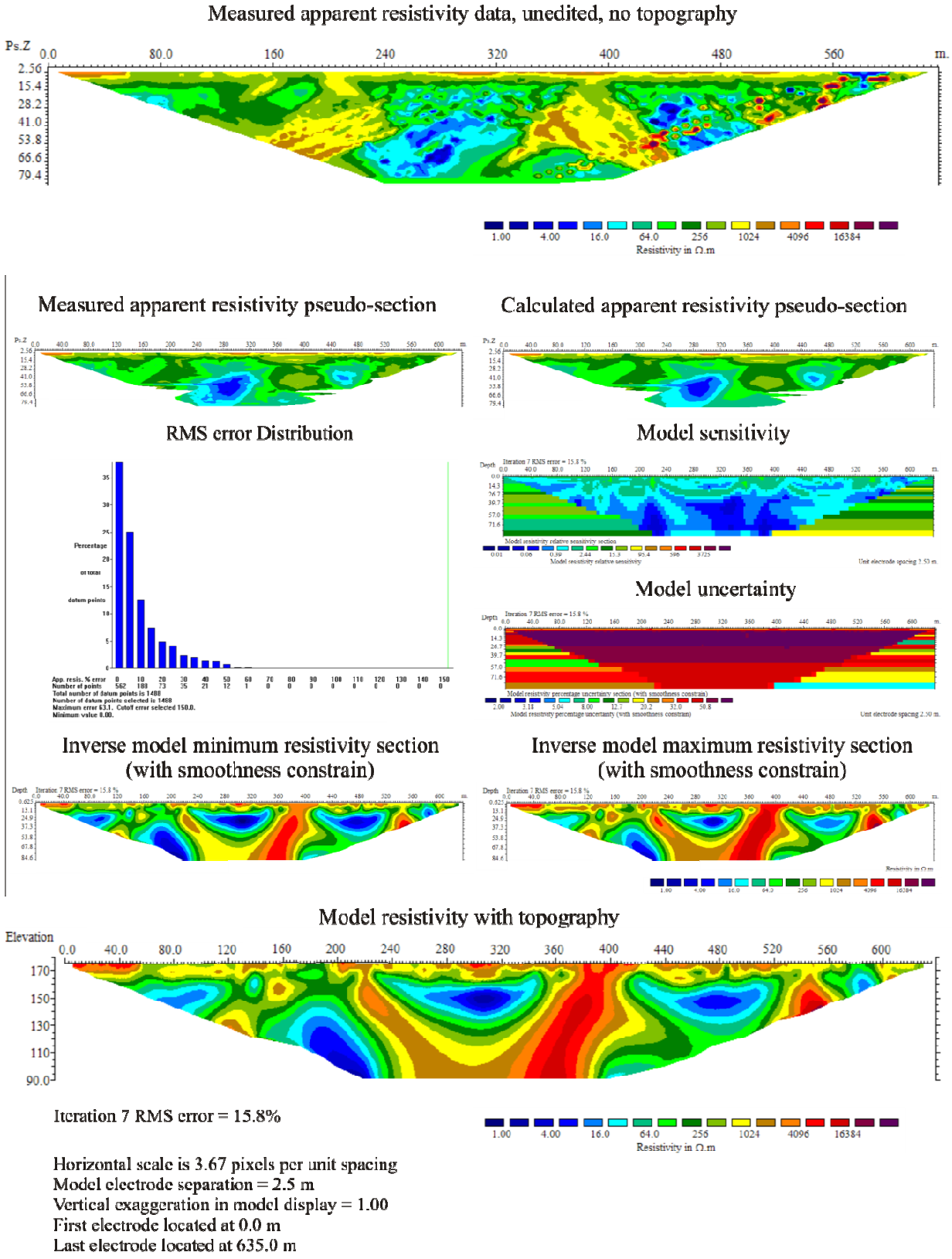


Figure 3.11: Pseudo-sections for Survey 1A

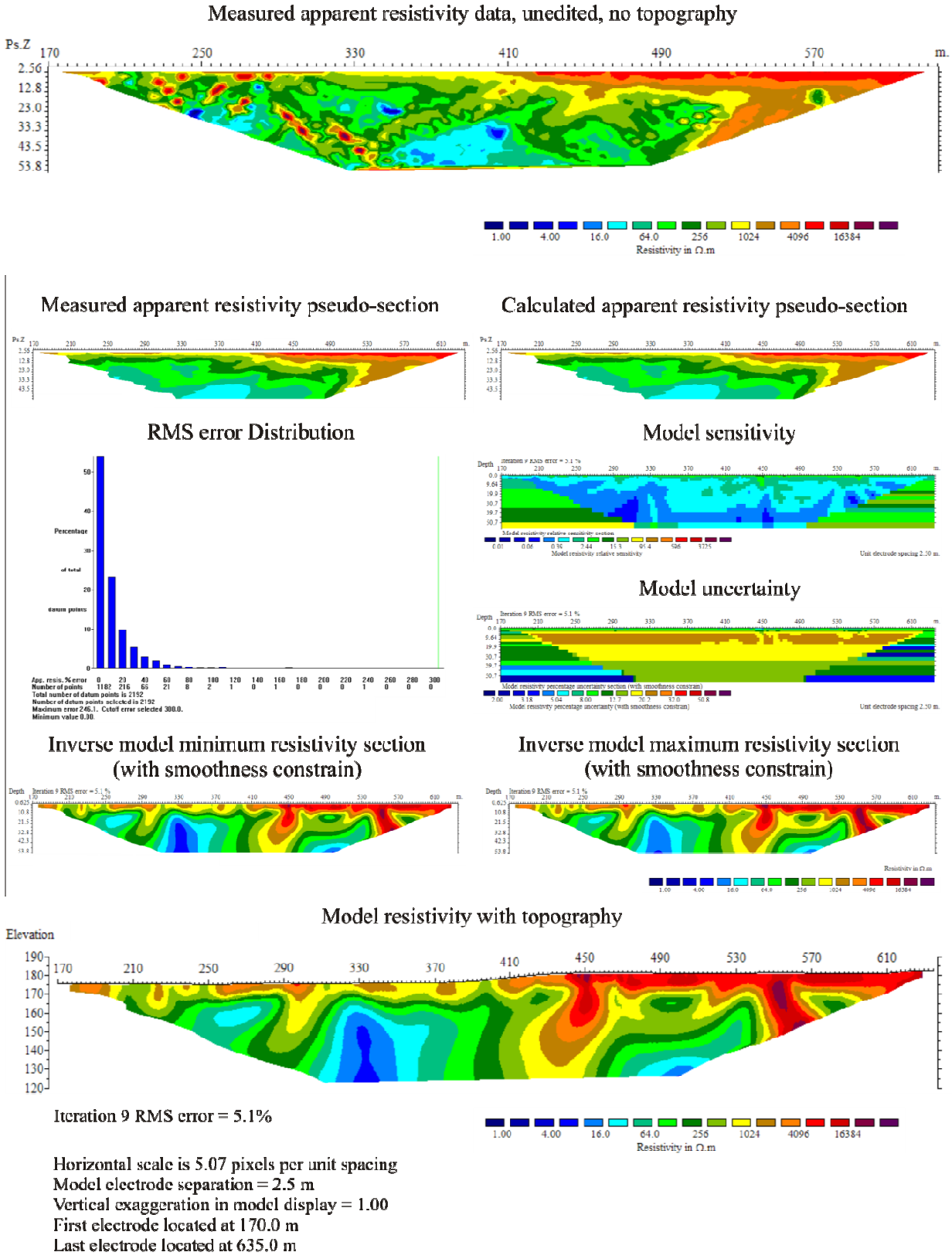


Figure 3.12: Pseudo-sections for Survey 1B.

3.3.4.3 Survey 1B

Figure 3.12 shows all pseudo-sections for survey 1B. Apparent resistivity values greater than 2000 Ω m (except near the surface) are anomalously high in the pseudo-section. These are displayed as orange to red to purple in the apparent resistivity pseudo-section. For the most part the bad data are removed, the exception being a cluster along the right edge. Inverted pseudo-sections produced significantly better results by leaving this data in than if it is removed. The artifact produced by the error during inversion is clear and simply excluded from interpretation.

3.3.4.4 Survey 2A

Figure 3.13 shows all pseudo-sections for survey 2A. Generally, this consisted of very good data, some errors arising from sticking electrodes, standout in the measured apparent resistivity pseudo-section, but is easily removed. A total of 2207 data points are retained for processing. The reason for better data was likely because of the ground conditions, survey 2A was in a recently ploughed paddock, with thick topsoil, allowing for easy placement of electrodes. Data was collected overnight where it rained sporadically but heavily. The saturated ground had the effect to improve the conductance of the ground at the surface. During data acquisition the bad electrodes causing the anomalous values were identified, cleaned with a wire brush on the takeout to remove any corrosion and watered several times with saline water. This did not improve the data suggesting that the error is related to the cable or the takeout as opposed to the ground conditions.

3.3.4.5 Survey 2B

Figure 3.14 shows all pseudo-sections for survey 2B. All electrodes have good ground contact in this survey. During data acquisition rain consistently fell so the ground was saturated, likely improving data acquisition considerably. Some noise is visible on the right hand quarter of the measured apparent pseudo-section. Most apparent resistivities are within 0-100 Ω m, however a small number were above 1000 Ω m, well above the normal range for this pseudo-section.

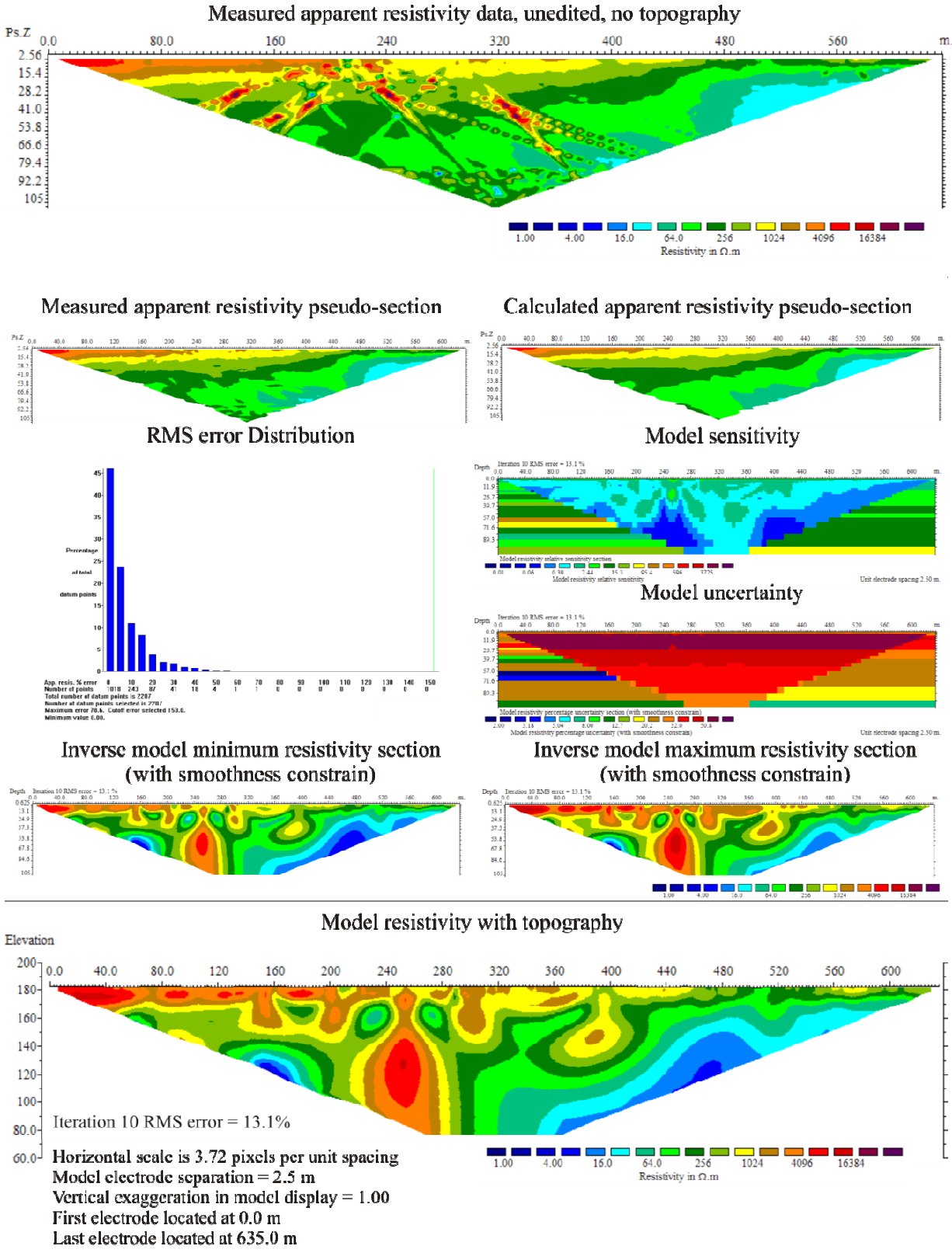


Figure3.13: Pseudo-sections for Survey 2A

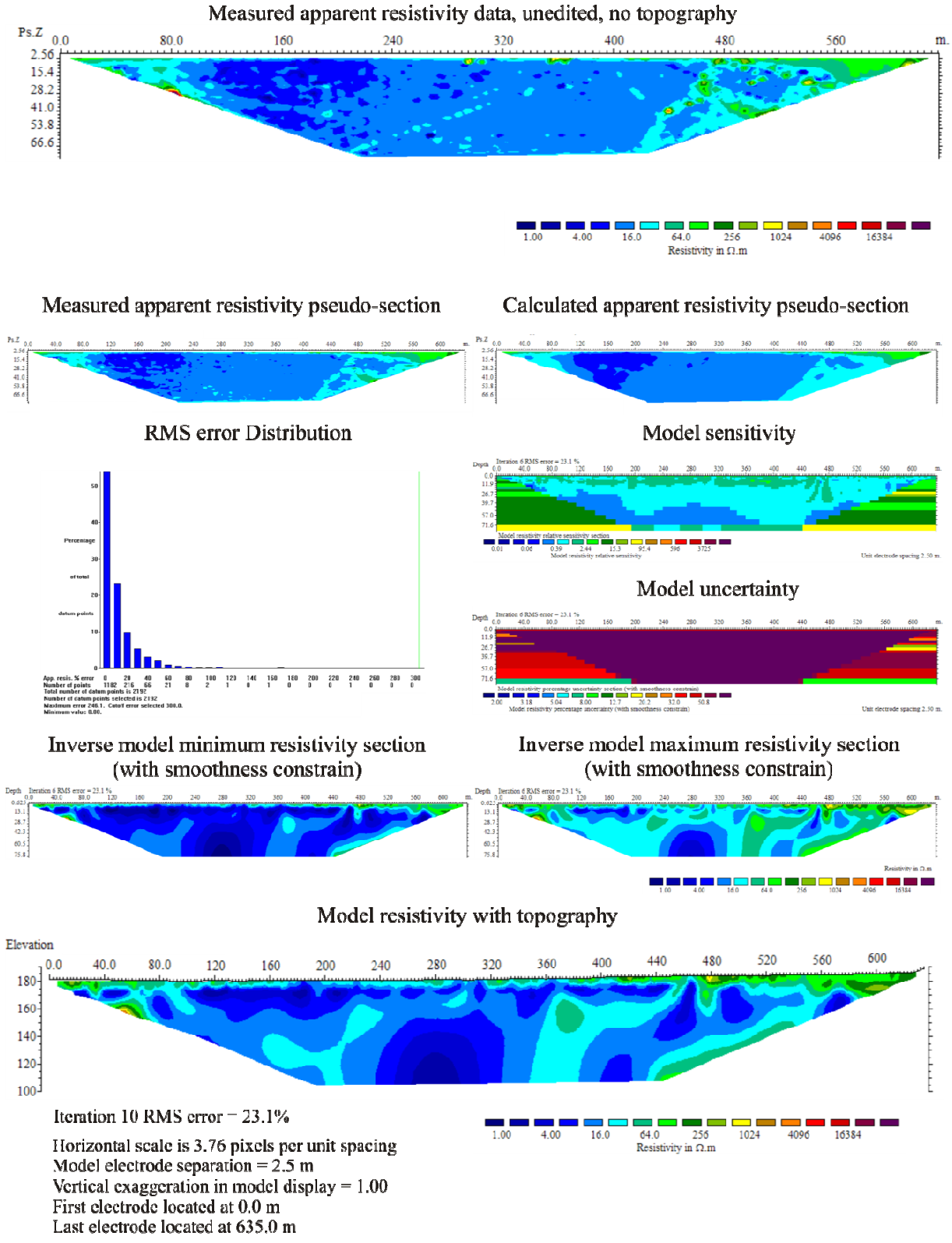


Figure 3.14: Pseudo-sections for Survey 2B

3.3.4.6 Line 3

Figure 3.15 shows all pseudo-sections for line 3. During the acquisition of the traverse data, there appeared to be higher than normal noise in the upper 2/3 of the pseudo-section. This was not apparent in the three previous roll-on files collected immediately prior to the traverse and the noise was much lower in the lower 1/3 of the acquisition. Ground conditions along the line were good but much drier than previous surveys. Thick topsoil made for easy placement of electrodes and good contact between the electrode and the ground. Corrosion could have built up on the clips and takeouts. Scratching the surface of the takeouts when connecting the electrodes appeared to minimize the effect of corrosion. The effect of the random data error is to increase the RMS of the pseudo-section indicating the difference between the measured and model apparent resistivities are greater in this pseudo-section compared to line 1 and line 2.

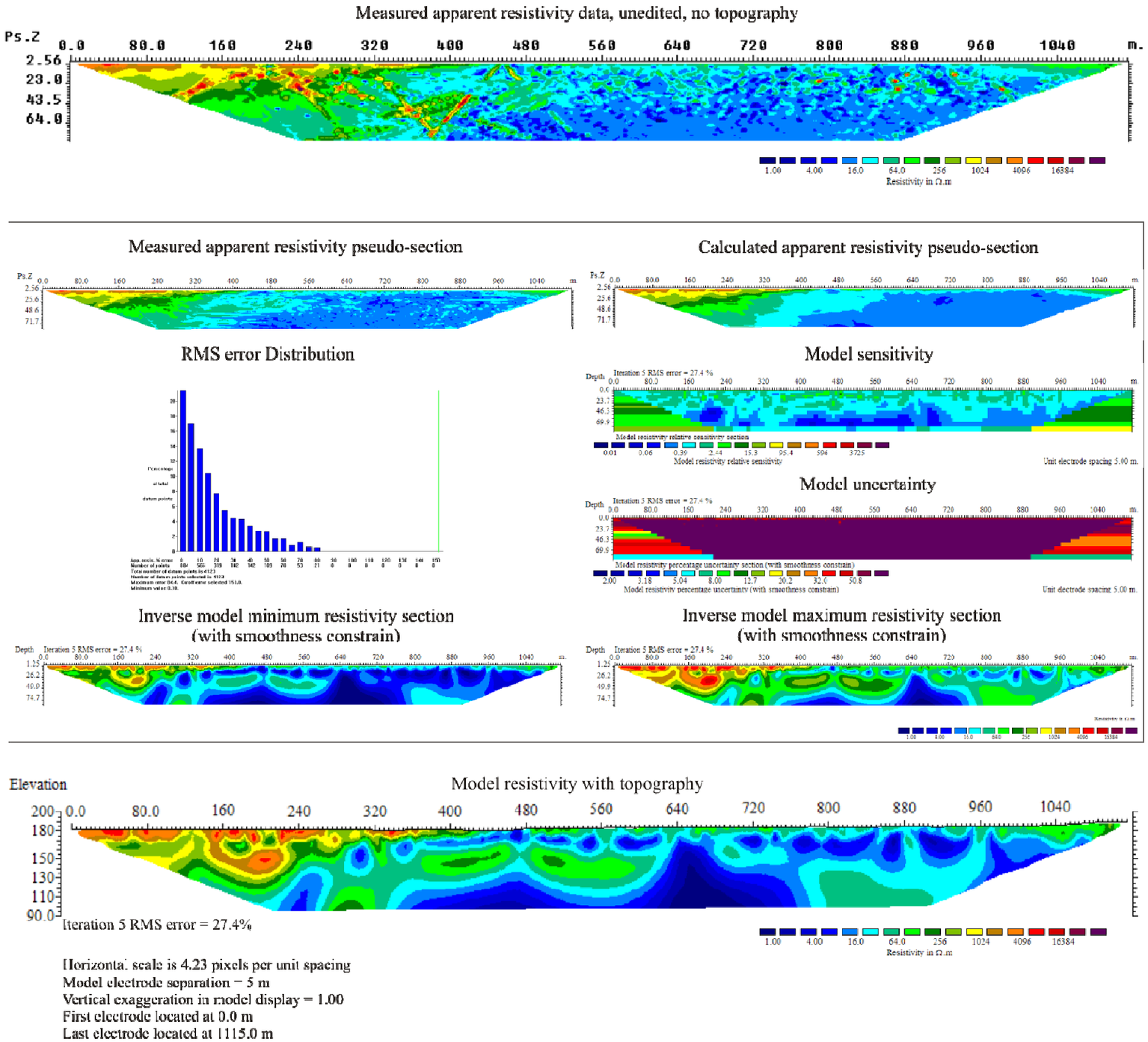


Figure 3.15: Pseudo-sections for Survey 3

3.4 Results and Interpretation

Figure 3.16 shows all inverted pseudo-sections for this study. All surveys are drawn at a 1:1 scale, separation between line 1 and 2 is accurate, separation between line 3 and line 2 is not representative of actual spacing but the alignment is. This allows for accurate comparison between the pseudo-sections and enables 3D interpretation of groundwater flow around the fault. The high resistivity band in line 1 between 200 m and 400 m, and the small sub-vertical band at 860 m, are the result of bad data that was not removed prior to inversion and does not reflect anything real in the subsurface. In profile 1A below about 20 m, good quality data on the margins of the error all have similar resistivities (less than 2 Ω m). This is supported by the conductivity measurements from well O28w/0219. Here below a depth of 25 m conductivity of the groundwater is above 5000 mS/m. It is a reasonable assumption that the good quality data at depth in profile 1A is representative of areas affected by anomalies in the inverted profile. Therefore, at depth, very low resistivities dominate the pseudo-section.

Below the lower terrace surface along line 1 is a band of moderate to high resistivity (500-4000 Ω m). 15-20 m below ground level is a relatively sharp boundary between the moderate to high resistivities and very low resistivities. The layer decreases in thickness slightly from northwest to southeast by approximately 8 m until about 640 m across where there it thickens again slightly until the terrace riser. This upper layer represents the Wairau Valley Aquifer situated within reworked Speargrass gravels. The undulating nature of the basal contact between reworked gravels and older Speargrass represents the Wairau River cutting into the older unit. They show a moderate to high resistivity because the gravel unit consists of less fines and a significantly greater hydraulic conductivity and water quality when compared to the older Speargrass gravels below.

Groundwater conductivity (Figure 2.2) measured during extension of O28w/0219 indicates that the upper 15 m consists of water with conductivities less than 300 mS/m reflecting the good quality water of the Wairau Valley Aquifer. From 16-25 m is a zone of brackish water between 3000 mS/m and 4400 mS/m. Below 25 m, groundwater conductivity is greater than 5000 mS/m.

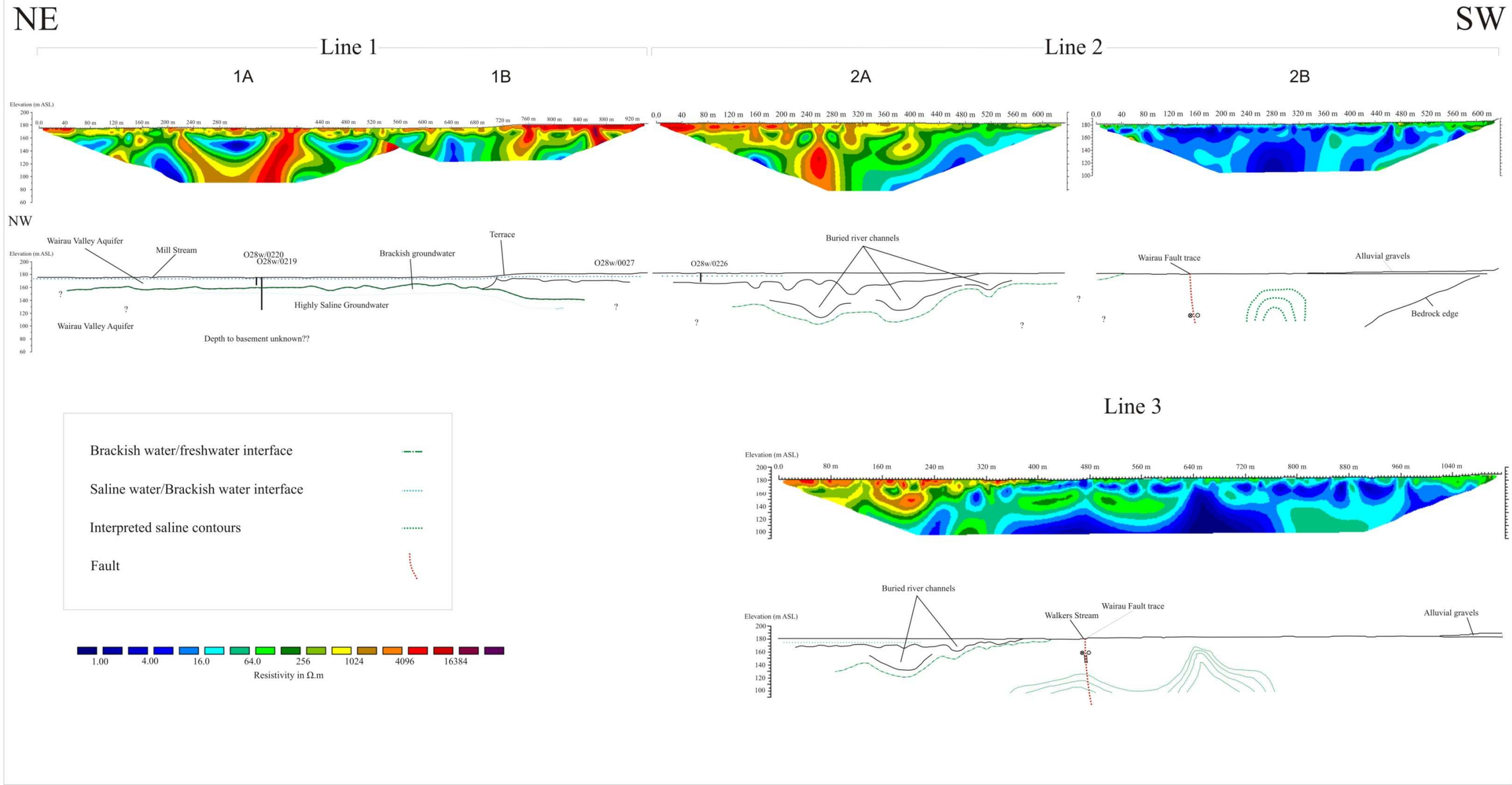


Figure 3.16: Interpretation of Wairau Valley Multi-Electrode resistivity surveys.

The marked difference between measurements at 13 m and 15 m suggests that the contact between the fresh water and brackish water is sharp. Furthermore, when well O28w/0220 was pump tested (Section 2.3.3) there was no increase in the conductivity of the water. From the bore log of O28w/0219 (Figure 2.2) and driller notes the change into higher conductivities correlates approximately with tighter gravels. Some mixing between saline/freshwater may occur within the Wairau Valley Aquifer but it is not considered significant due to the hydraulic properties of the older unit and a downward flow gradient here. The zone of brackish water present between 16-25 m is thought to result from mixing between deep saline water and downward moving Wairau Valley Aquifer water into the Speargrass Gravels. This zone is present on the line 1 pseudo-section between 16-25 m at O28w/0219 and is consistent laterally across the pseudo-section until the terrace riser. Past this point, it is difficult to define this zone as the boundary becomes more complicated, but some degree of mixing is likely at any saline/freshwater boundary. At O28w/0219 a second sharp change in the conductivity values occurs at 25 m. Below this level the saline water has a higher conductivity than sea water. Figure 2.? Shows some variation in the highest conductivity values but a gradual increase with depth can be inferred which would be expected, although the measured values are thought to be close to maximum salinity, it is difficult to know without sampling at greater depths.

Because water density increases with salinity it is likely that the saline water extends to basement although this cannot be known without actually imaging the basement in the resistivity surveys. The maximum depth in the resistivity surveys, however, is approximately 80 m ASL, basement is not expected to be much lower than this.

The highest resistivity values occur behind the Speargrass terrace riser, as a wedge tapering out to the south. The wedge extends approximately 200 m into survey 2A at resistivities greater than 4100 Ω m. Across survey 2A surface values decrease from northeast to southwest. This is a result of the gravels behind the terrace.

Within 2A are several circular features between 10 m and 30 m depth are present just below the high resistivity surface values. The resistivity values fall within the same contour intervals as the Wairau Valley Aquifer. The shape and size of these areas suggest that they could be old river channel deposits. Channel deposits generally have a higher hydraulic conductivity than

surrounding strata, therefore there is potential that these channel deposits could be water-bearing which would explain the similarity to the Wairau Valley Aquifer. This is also interesting because of the water deficit that exists from the southern hills waters either side of the fault and could potentially account for this and could explain the higher than expected transmissivity values from the O28w/0226 pump test.

The areas of very low resistivity values in survey 2A are at depth and on the margins of the survey. Similar low values on the southwest and northeast margins of 1B and 2A, respectively, occur at the same depth. The area of low resistivity on the southern edge is clearly dropping in elevation with distance from the fault. There are several possible reasons for this, firstly the saline water could be seeping through the fault from the southern side from an area of high concentration to low concentration, and possibly higher water pressure due to an upward flow gradient, with the fault acting as a semi-permeable barrier to groundwater flow. Secondly, series of splay faults on the northern side of the fault which do not reach the surface could allow saline water move upward to the point where the splay terminates in the subsurface. A seismic survey would determine any structure in the subsurface gravels. Although the presence of splay faults in the Speargrass Gravels is likely, there is no evidence that they have a significant effect on the subsurface saline groundwater distribution. The apparent drop in elevation of the saline water in the subsurface could be controlled by the hydraulic conductivity variation which is likely present in outwash deposits and a freshwater source to flush the gravels of any residual salinity. Where there are high hydraulic conductivities, e.g. paleo-channels with fresh water recharge source salinity will be diluted and dissipated over time. Areas where the gravels are tighter with a very low hydraulic conductivity can retain the saline component for very long periods.

Survey 2B is dominated by very low resistivity values throughout the pseudo-section suggesting that the area is dominated by saline water. The areas of highest resistivity occur at the surface at each end of the pseudo-section and along its southern edge. The surface trace of the Wairau Fault crosses survey 2B approximately 90 m south of the beginning of the profile, Trench logging by Zachariasen, et al (2006), indicates the fault dips 85^{o} south in this region. There are no obvious resistivity variations near the trace of the fault which might be expected from a major fault trace. This may be a consequence of the array type used in this survey. The Wenner method does not detect horizontal variations in resistivity as well as it detects vertical changes (Loke, 2004).

Because the fault trace is sub vertical, any changes in resistivity either side of the Wairau Fault may not be seen in the pseudo-section. Furthermore because there is no lithological change either side of the Wairau Fault and saline groundwater is assumed the major influence on subsurface resistivity, MER surveys are not likely to pick up any change unless groundwater chemistry was significantly different either side of the Wairau Fault. The very thin wedge of moderately higher resistivity values corresponding with a change in slope are thought to represent the survey crossing part of a low angle fan from the Hillesden Stream leading into a small depression behind the fault. On the northern side of the fault is a small mound less than 1 m in height, this is probably remnant of the northern side forming the hanging wall here. Survey 2B extends to the base of the Southern Hills. A series of moderately higher resistivities compared to the majority of 2B data are situated along the edge of the survey at an angle of approximately 20^{o} from horizontal to the northeast which most likely represents the bedrock edge of the valley to depth. At no point does it begin to level out, giving no indication of the basement depth in the valley. The lowest resistivities in the pseudo-section are present at its base in the center and appear to radiate from depth. This could represent saline water migration along the Wairau Fault and related secondary fractures in the basement. Structures in a pseudo-section at depth can be misleading, however, and not a representation of subsurface properties.

Line 3 runs parallel to line 2 and shows several similarities. The Wairau Fault trace is inferred from the surface mapping, the surface trace is defined by Walkers Stream (Figure 3.10) which crosses the survey approximately 480 m from the northwestern end of the line. The fault trace in the pseudo-section suggests the fault is influencing the groundwater at depth. The low resistivity contours around the fault are concave in form at the point of the fault trace and move out into the northern side of the fault, suggesting possible upward flow of saline water along the fault in the Speargrass Gravels. The low resistivity contours present at the base of survey 2B, are also visible in line 3. The distance from the fault to the core of the low resistivity contours is equal for both 2B and line 3. The form of the contours suggests a plume of saline water rising from depth between the Wairau Fault and the Southern Hills, the most likely source is the fault itself allowing water to move upwards from depth. This feature correlates well with a similar feature in 2B, therefore, it is likely to be representative of actual ground conditions as opposed to an artifact of inversion. This could only be confirmed by drilling a well into the area of lowest resistivity values south of the Wairau Fault to determine the groundwater chemistry and the

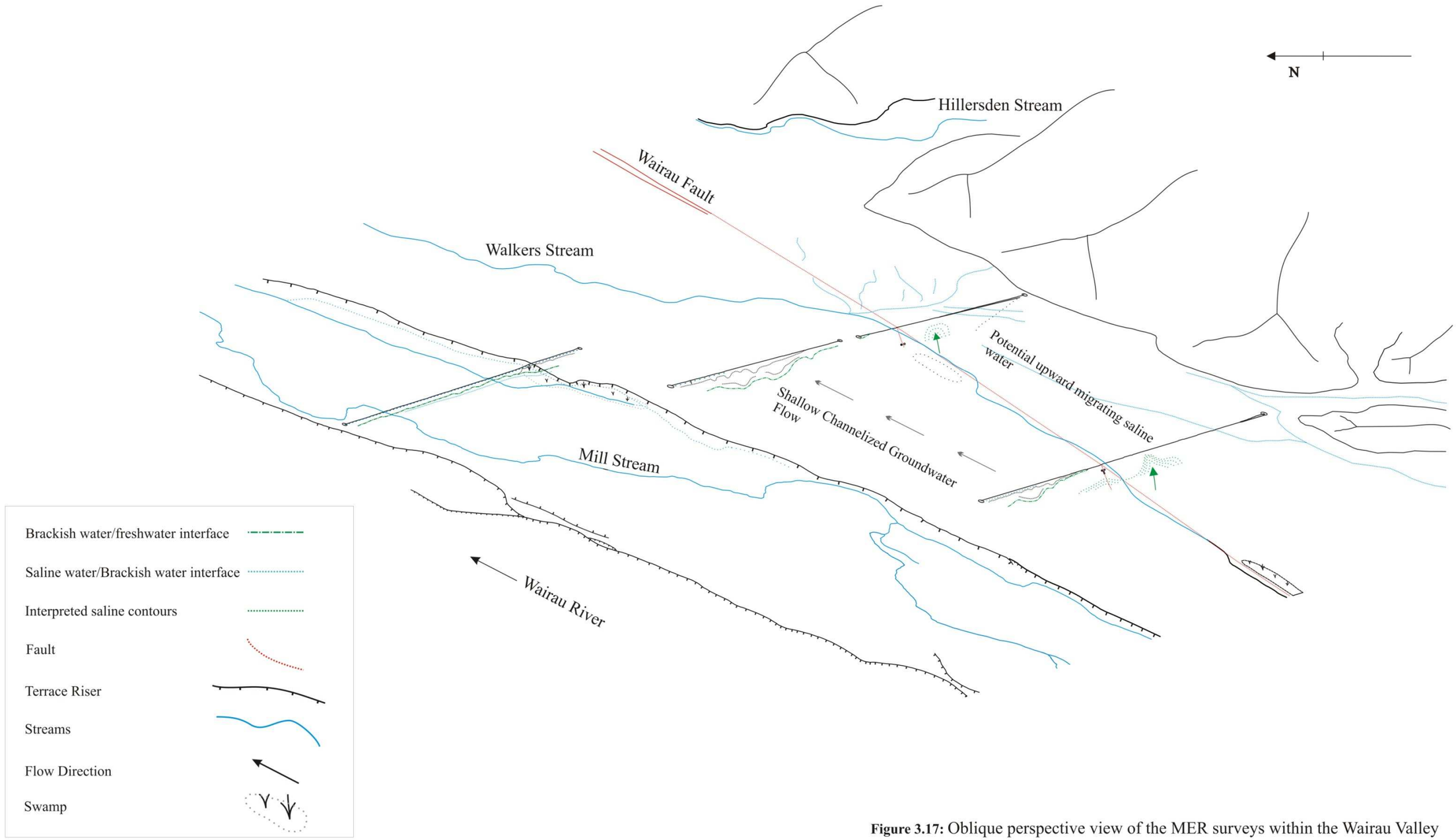


Figure 3.17: Oblique perspective view of the MER surveys within the Wairau Valley

variation of static water levels with depth. Line 3 points into a small valley in the Southern Hills, as a result bedrock will be deeper below this line compared to survey 2B, for this reason bedrock is not present in line 3.

Northeast of the Wairau Fault Line 3 and Survey 2A show almost identical features. Figure 3.17 is an oblique perspective view of the Hillesden area with all surveys in their correct locations relative to surface features. From this, linear trends can be inferred from matching features between line 2 and 3. The Wairau Fault trends at an angle of approximately 075^{o} from north, the major terrace trends at 063^{o} close to line 3 and begins to bend around to a more northeast direction just past line 2. The inferred channel deposits run sub-parallel to the major terrace riser and, if continues on a similar trend, it would intersect the fault giving the buried channels a fresh water source.

The inferred saline upwelling feature in line 3 and survey 2B is approximately equal distances from the Wairau Fault in each survey and it is likely linked to this structure at depth most likely where the Wairau Fault enters bedrock.

3.5 Chapter Summary

The MER surveys in the Wairau Valley supports the previous ideas on the Wairau Valley Aquifer depth and lateral extent and indicates the salinity is ubiquitous at depth below the lower terrace surface. The area between the Southern Hills and the Wairau Fault is dominated by saline groundwater, low resistivity contour at depth infer saline water is most likely entering the valley through the Wairau Fault from depth although more fieldwork would be required to confirm this. The most important factor on the depth to the saline water is thought to be the hydraulic conductivity of the gravel and a recharge source, this is proposed to explain the high resistivity features at depth in survey 2A which are interpreted to be buried river channel deposits recharged by Southern Hills water.

CHAPTER FOUR

Isotope Analysis

4.1 Introduction

Chapter four introduces the isotope data for the saline water at O28w/0219. Samples collected for this study are analysed in conjunction with the previous data collected by the Marlborough District Council. The use of stable isotopes of oxygen, hydrogen, and carbon (^{18}O, ^{2}H and ^{13}C) will give insight into the original source of the saline groundwater and define any mixing trends between different waters, if present. Radioactive isotopes of hydrogen and carbon (^{3}H, and ^{14}C) as well as Sulphur hexafluoride (SF_6) and Chlorofluorocarbons (CFC) have been sampled from O28w/0219. With this data, it is be possible to determine when the saline water was last at the surface. This is important in understanding the paleo-physiographic setting present at this time that may have lead to the high salinity. Pleistocene glacial cycles, relative sea level fluctuations, depositional facies of the Wairau River, and the climatic setting will all influence the nature of the water in their environment.

4.2 Stable Isotope Data

The use of stable isotope analysis is common in groundwater studies to identify the source of surface and groundwaters. Isotopes are variations of a particular element which differ by the number of neutrons and thus the atomic weight (Drever, 1997). The difference in mass can result in fractionation between two isotopes of an element by various biological, chemical or physical processes, the later includes evaporation and condensation which are fundamental processes in the hydrological cycle. Chemical processes become important in groundwater where long residence times allow significant water rock interaction to take place. Stable isotopes of carbon are significantly affected by biological fractionations during photosynthesis.

Stable isotope values are reported as the relative difference (δ_x) per mil (‰) between the sample ratio (R_x), for example, $^{18}O/^{16}O$, and the same ratio of a certain standard (R_{std}), this is given by the equation [4.1] (Hem, 1992):

$$\delta_x = \left[\frac{R_x - R_{std}}{R_{std}}\right]1000 \qquad [4.1]$$

4.2.1 $\delta^{18}O$ and δD

Common isotopes used in groundwater studies are oxygen isotopes (^{18}O, ^{16}O), and the hydrogen isotopes (^{2}H, ^{1}H), the heavier isotope for hydrogen (^{2}H) is generally referred to as deuterium (D). The common isotopic standard for hydrogen and oxygen is *Vienna Standard Mean Ocean Water* (V-SMOW). Deep ocean water has a stable isotopic composition and by definition of SMOW $\delta^{18}O$ and δD values are equal to zero. Minor fluctuations at the surface via evaporation and freshwater influxes can produce slightly positive or negative $\delta^{18}O$ and δD rvalues, however, this creates only small variations by several ‰ (Faure & Prior, 2005).

The $\delta^{18}O$ and δD value varies considerably in precipitation and is almost always depleted in ^{18}O and D compared to ocean water. Craig (1961) first identified that the $\delta^{18}O$ and δD composition of rain data from around the globe was related along a linear regression, this is termed the Global Meteoric Water Line (GMWL), $\delta^{18}O$ and δD are related by:

$$\delta D = 8(\delta^{18}O) + 10 \qquad [4.2]$$

For New Zealand precipitation, Stewart and Taylor (1981) suggest an intercept value (10 in equation [4.2]) of 13‰. However, a value of 10‰ is still used in this study as it fits better with the data in the Wairau Valley and has been used in the previous groundwater studies in the Wairau Valley and on the Wairau Plains.

The two major factors controlling the isotopic signature of precipitation is the temperature (seasonal variations) and the composition of atmospheric water vapour at the time of precipitation. During evaporation the heavier isotopes (^{18}O and D) are enriched in the residual fluid which, in the case of the hydrological cycle, is the ocean. This means that atmospheric water has slightly negative $\delta^{18}O$ and δD values relative to ocean water. As air masses move

progressively inland, condensation causes precipitation the heavier isotopes are enriched in the rain drops causing the water in the atmosphere, still in gas phase, to become depleted in ^{18}O and D as it progresses inland, this is known as Rayleigh Fractionation (Drever, 1997). Isotopic composition varies on a regional scale due to altitude, latitude, the continental effect (distance from the ocean source). $\delta^{18}O$ and δD ratios both decrease with increasing altitude and latitude, however, this is complex in the case of altitude in inland ranges and on the leeward side of mountains. Latitude and the continental effect are largely controlled by Rayleigh Fractionation causing progressively lower $\delta^{18}O$ and δD values. The quantity of rain also acts to lower $\delta^{18}O$ and δD values (www.usgs.gov, 2008).

Figure 4.1 indicates the possible areas a sample may plot on a $\delta^{18}O$ vs. δD plot relative on the source of the water. The mantle $\delta^{18}O$ ratio is approximately +5.7‰, the $\delta^{18}O$ ratio of a rock is largely dependent on its silica content, for example, mafic rocks are only slightly higher than mantle ratios, granite is above +10‰. The $\delta^{18}O$ ratio in sedimentary rocks is directly controlled by the temperature at which the rock formed. Low temperature formation will produce higher $\delta^{18}O$ ratios, carbonates can have a $\delta^{18}O$ ratio up to +30‰ (Faure & Prior, 2005).

Clayton *et al*., (1966) suggests four processes which may alter the δD within a basin:

- Variation in the climatic conditions altering the δD value for precipitation in the basin.
- Deuterium exchange between hydrocarbons, hydrated minerals, or hydrogen-sulphide.
- Fractionation of hydrogen isotopes due to evaporation leads to the residual fluid enriched in the heavy deuterium relative to the initial water.
- Diffusion between the heavy and light hydrogen stable isotopes.

Of these processes evaporation and climatic variation are considered the most important.

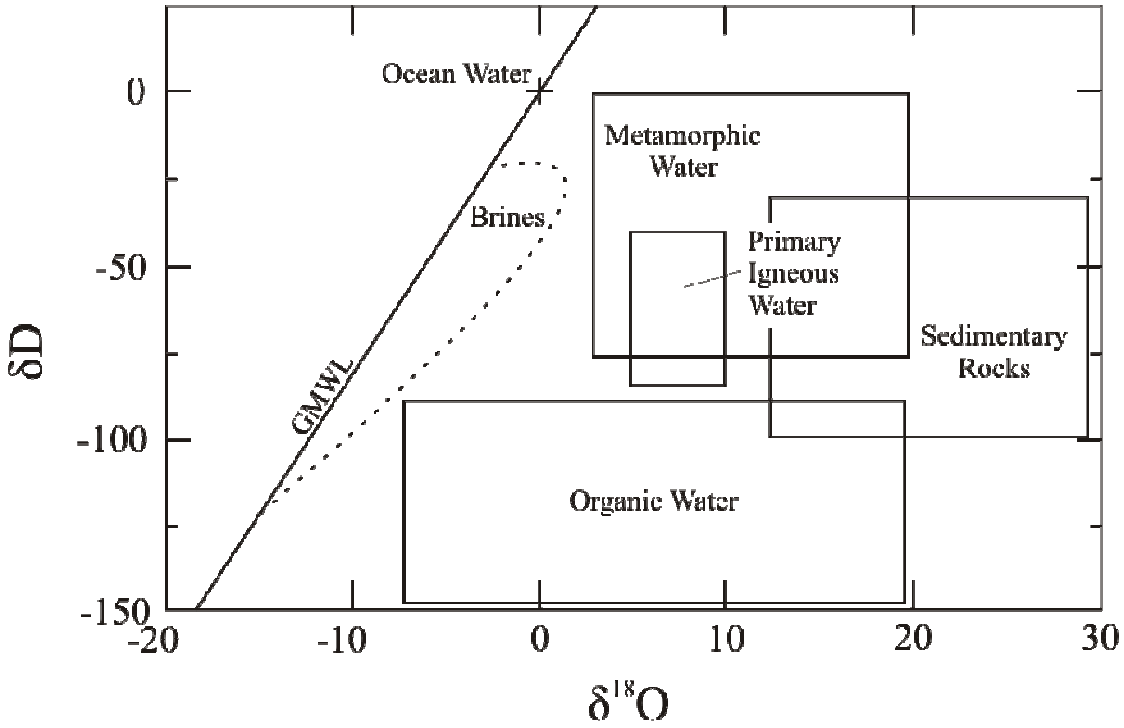


Figure 4.1: A general compartmentalisation of potential source fluids relative to their δD vs. $\delta^{18}O$ values, modified from Shepard (1986).

The area on the graph which Shepard (1986) suggests is indicative of a brine is much too simplified. Several potential fractionation process could result in a sample plotting in this area, for example, kinetic fractionation of meteoric water, meteoric water which has undergone subsequent ^{18}O enrichment through interaction with rock, or a mixing between meteoric water and a secondary water with a different stable isotope. Regression line analysis can help to differentiate between these potential sources. A positive regression of three to five is characteristic of kinetic fractionation associated with evaporaition (T. Horton, pers. Comm., 2008). It is common for meteoric water to mix with waters from a different source. This would lead to a regression line between the two end members involved, for example seawater mixing with meteoric water would show a regression line between the different signatures of each end member. Rocks contain almost no hydrogen, therefore, waters influenced by water rock interaction processes over extended time periods generally plot along a horizontal line to more positive $\delta^{18}O$ ratios reflecting the ^{18}O rich nature of rocks (Payne, 1988). This is common for deep circulating hydrothermal water derived from meteoric water.

4.2.2 $\delta^{13}C$

Carbon isotope analysis is reported relative to the PDB standard. This standard originates from early stable isotope analyses of carbonates which used powdered samples of a belemnite (*Belemnitella americana*) from the upper Cretaceous Peedee Formation in South Carolina as the reference standard. By definition the $\delta^{13}C$ value of PDB is zero (Sharp, 2007).

Figure 4.2 show the $\delta^{13}C$ values attributed to various stages in the carbon cycle. Generally rivers have $\delta^{13}C$ values similar to atmospheric ratios. Shallow ocean water is close to 0‰, however, this does vary by approximately 1-2‰ at local scale. Carbon derived from organic material is significantly more negative than seawater. The degree to which the carbon is fractionated is related to the physiologic processes which incorporate the CO_2 into the plant. C_3 plants metabolise CO_2 through the calvin cycle. $\delta^{13}C$ from C_3 plant ranges between -23‰ to -34‰, with a mean of -27‰ (Faure & Mensing, 2005). C_3 plants are favoured in higher latitude areas where cooler climatic conditions exist. Most trees, herbs, cool weather grasses are C_3 type (Sharp, 2007). C_4 plants, the second most common type, use hatch-slack process to metabolise CO_2. C_4 plants include maize, tropical grasses, salt marsh and desert plants. $\delta^{13}C$ from C_4 plants is between -6‰ and -23‰ with a mean of -13‰.

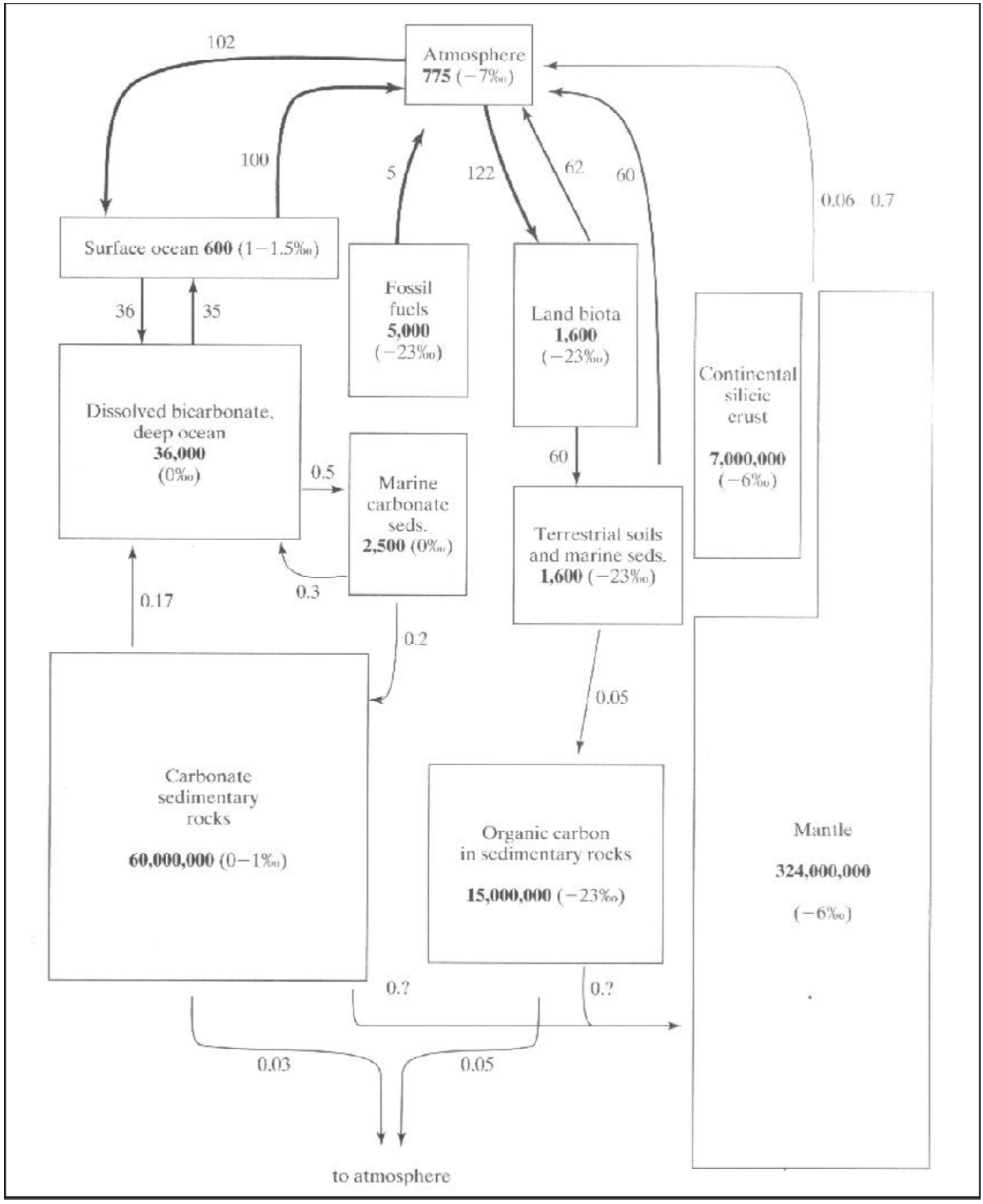


Figure 4.2: Carbon Cycle showing approximate $\delta^{13}C$ for various stages. (Sharp, 2007)

4.3 Radioactive Isotope

4.3.1 Tritium

Tritium (^3H) is a rare hydrogen isotope with a half life of 12.3 years. One tritium unit (TU) consists of one T atom per 10^8 H atoms. Small concentrations occur naturally in the atmosphere where cosmic rays interacting with nitrogen and oxygen ions, however, the most significant source is from thermonuclear weapons detonated between 1952 and 1969 resulting in a massive spike in the atmospheric concentrations between this time (Drever, 1997). Atmospheric tritium concentrations in New Zealand rainfall since 1940 are shown in Figure 4.3.

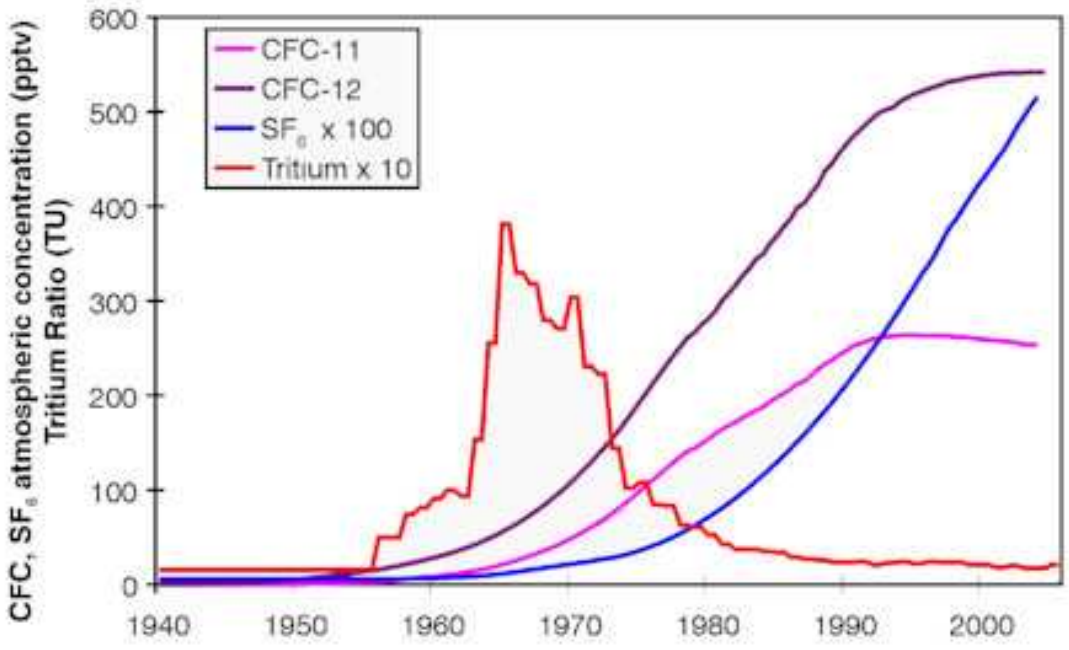


Figure 4.3: CFC, SF_6, and tritium ratio atmospheric concentrations in New Zealand rainfall since 1940 (www.gns.cri.nz, 2008).

Natural pre-bomb rainwater levels were between 5-10 TU, however, the exact number is uncertain due to minimal data collected (Drever, 1997). Atmospheric peak tritium concentrations shown in Figure 4.3 are somewhat irregular, this leads to ambiguous ages from tritium analysis alone. For this reason CFC-11, CFC-12, and Sulphur Hexafluoride (SF_6) are often tested concurrently to constrain the tritium age values (www.gns.cri.nz, 2008). Age ranges for the four major age dating methods used in this study are shown in Figure 4.4.

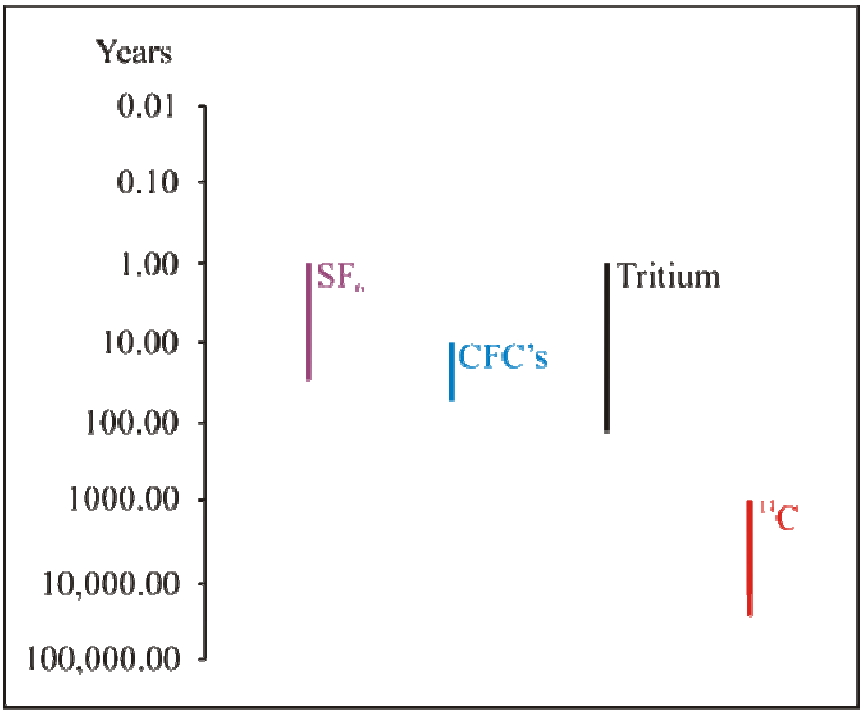


Figure 4.4: Age ranges for methods of groundwater age dating used in this study, modified from (www.gns.cri.nz, 2008).

Manzor (1991) suggests the constraints shown below to infer an approximate age range from tritium data:

- Less than 0.5 TU represents water pre 1952,
- Greater than 10 TU represents water post 1952,
- Where tritium concentrations are between 0.5-10 TU the water is probably a mix between pre-1952 and post-1952 waters.

4.3.2 Chlorofluorocarbons

Chlorofluorocarbons (CFC's) are derived from an anthropogenic in origin and do not occur naturally. In the past they have been used for refrigeration and pressurisation of aerosol cans. Since the 1940's CFC's have gradually increased until the 1990's (Figure 4.3) where they were slowly phased out due to their effects on ozone depletion. This means that CFC's are not useful where recharge is younger than 1990. CFC's can be modified in several ways when in the groundwater system that can lead to ambiguous age dates, these include (Stewart & Morgenstern, 2001):

- Reduction of CFC's from microbial degradation in an anaerobic environment,
- Local anthropogenic contamination,
- Solubility varies with temperature, therefore, error in the estimated recharge temperatures can lead to incorrect age dates.

4.3.3 Sulphur Hexafluoride

Sulphur Hexafluoride (SF_6) does occur naturally but is predominately anthropogenic in origin and has been increasing in atmospheric concentration since the 1960's (Figure 4.3). SF_6 has a very long residence time in the atmosphere (800-3200 years). SF_6 is relatively conservative compared to CFC's and is generally not modified in groundwaters (Vincent, 2007).

4.3.4 Carbon^{14}

Carbon^{14} (^{14}C) is present in the atmosphere from the same sources as tritium, cosmic rays interacting with nitrogen and by nuclear bombs in the 1960's and 1970's, however, the input from nuclear explosions is significantly less relative to the ambient atmospheric concentrations compared to tritium and is less of a factor. ^{14}C has a half life of 5,730 years and can date waters up to a theoretical minimum age of 50,000 years (Figure 4.3), however, in practise the actual minimum age is closer to 30,000 years before present (Drever, 1997).

^{14}C is removed from the atmosphere through precipitation then infiltration into the groundwater system. Once ^{14}C is isolated from the atmosphere it begins to breakdown to nitrogen^{14} (^{14}N) by radioactive decay. The amount ^{14}C degrades over time is derived from the equation below:

$$(^{14}C)_t = (^{14}C)_0 e^{-kt} \qquad [4.3]$$

Where: $(^{14}C)_t$ = the amount of ^{14}C present at time t

$(^{14}C)_0$ = the amount of ^{14}C present a t = 0

k = decay constant

The decay constant is related to the half-life $T_{1/2}$ given by the equation:

$$t_{1/2} = \frac{\ln 2}{k} \qquad [4.4]$$

To calculate the time the water was last in contact with the atmosphere CO_2, $^{14}C_0$ must be known. This is derived from tree ring calculations from the last 7000 years. Prior to 7000 years B.P. the $\delta^{14}C$ value is assumed constant, no accurate measurement is available at this time to determine concentrations prior to this time (Drever, 1997).

Dating groundwater using ^{14}C can have significant uncertainty because the dissolved inorganic carbon (DIC) could potentially be a mix from several different sources. Corrections to this are generally based on mass balances of the ^{13}C or major chemical constituents (Zhu & Murphy, 2000). Several model are in the literature to define the age depending on the mass transfer reactions present (Fontes & Gardiner, 1979: Mook, 1980). Corrections require an assumption of the specific mass transfer reactions that may have affected the groundwater, for example dissolution or precipitation. No mass balance model in the literature is applicable in all situations and a more site specific approach is required to develop applicable ages (Zhu & Murphy, 2000).

4.4 Stable Isotope Analysis of Wairau Valley Waters

Stable isotope samples were collected by the Marlborough District Council and analysed by Geological and Nuclear Sciences (GNS) at O28w/0219 (50 m). These results are compared to earlier analysis completed by Taylor (2003) for the Marlborough District Council which sampled δ18O and δD selected wells and streams on the south bank of the Wairau River. There is only one $\delta^{13}C$ sample in the study area.

4.4.1 $\delta^{18}O$ and δD.

The $\delta^{18}O$ and δD values of the Wairau River has been defined by earlier work in the study area and on the lower Wairau Plain by Taylor *et al*, (1992) and Taylor (2003). These concluded that the most representative $\delta^{18}O$ composition of Wairau River water is 8.68 ± 0.003, therefore, the Wairau River $\delta^{18}O$ value of -8.61 in Figure 4.5 is considered as a good representation of average Wairau River composition. The Wairau River sample of $\delta^{18}O$ = -8.21 is possibly reflecting the variation in the oxygen isotope signature of Wairau River water observed in previous studies. The three samples analysed for O28w/0219 (Table 4.1) show little variation over the eight month period for $\delta^{18}O$ ratios indicating that the values are probably representative of deep saline groundwater at O28w/0219.

Table 4.1: $\delta^{18}O$ and δD data collected for O28w/0219 since extension to 50 m.

Well Number	Sampling Date	$\delta^{18}O$	δD
O28w/0219	9/5/2007	-4.35	-46.6
O28w/0219	4/7/2007	-4.45	-
O28w/0219	23/1/2008	-4.41	-

Figure 4.5 shows the data from O28w/0219 plotted with the data from Taylor (2003), including selected saline and non-saline wells between the South Hills and the Wairau River. Appendix 4.1 contains $\delta^{18}O$ and δD values for all well and stream samples collected prior to this study.

Shallow groundwater on the south bank of the Wairau River below the Wr1 terrace surface is controlled by Southern Hills runoff, stream samples plot along an evaporative trend from Southern Hills groundwater samples (Taylor, 2003).

All saline samples from the Wairau Valley plot along a positive enrichment regression ($R^2 = 0.972$) with a slope of 3.4 from the average Wairau River composition. The strong positive fit for all saline samples suggest a common source of fractionation. Two sources are considered which could give rise to this regression, firstly, kinetic fractionation through evaporation of Wairau River water or a mix between two end member waters, one known to be Wairau River water.

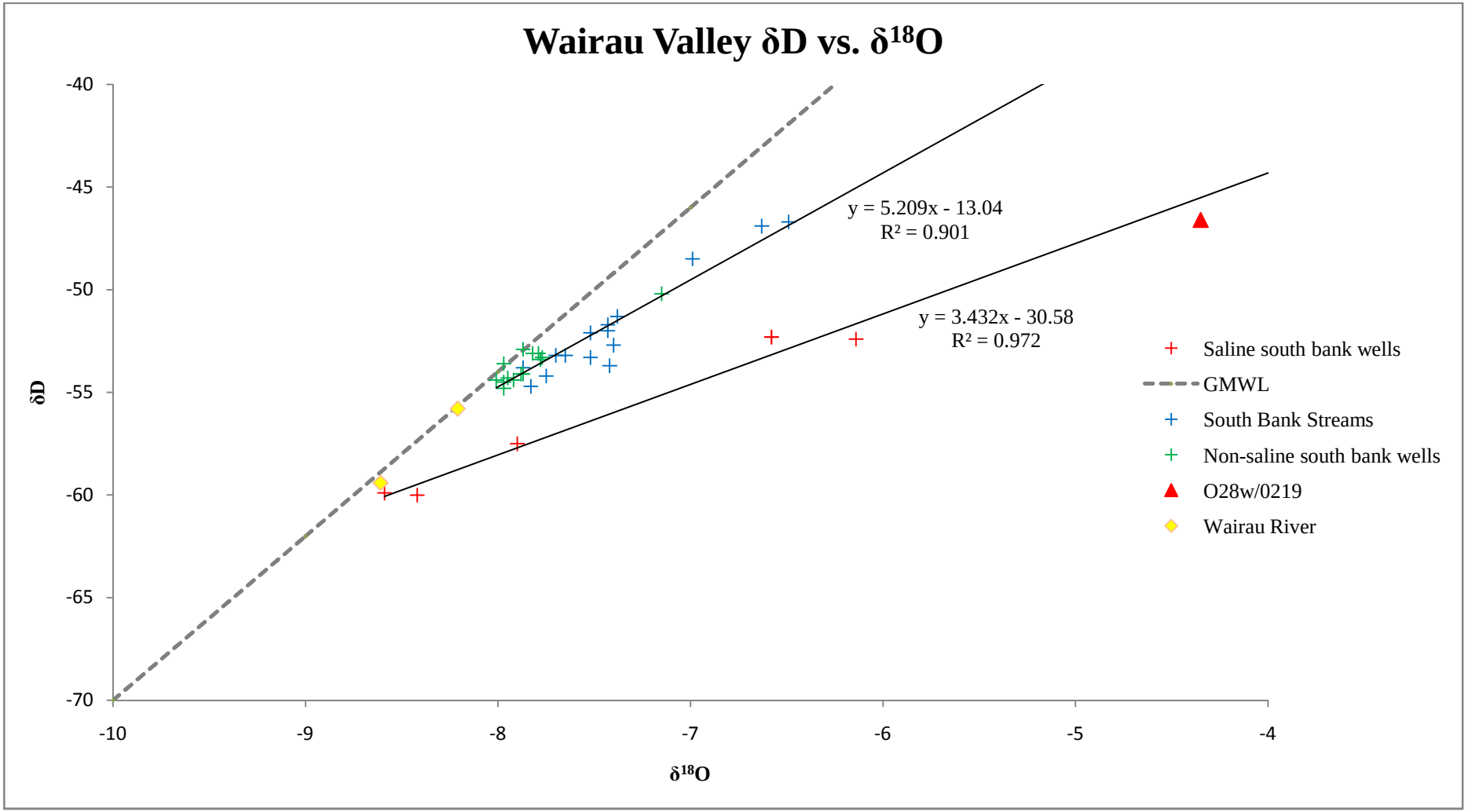


Figure 4.5: Wairau Valley δD versus $\delta^{18}O$, Data is from Taylor (2003) except for well O28w/0219, GMWL from Craig (1961)

The trend line for the saline samples is characteristic for kinetic fractionation by evaporation. Chloride concentrations show a positive correlation with $\delta^{18}O$ ratios (Figure 4.6), however, the relationship between chloride and $\delta^{18}O$ does not plot on a straight line which would be expected for evaporative concentration. Figure 4.6 suggests that chloride concentration increases exponentially with later stage isotope fractionation. It is difficult to make an accurate interpretation of the relationship between $\delta^{18}O$ and chloride due to the small sample set. More data would help define the relationship more accurately as data are bias towards high and low chloride concentrations. The R^2 value of 0.972 is very close to 1, however, this may reflect the low number of samples. The samples which have chloride concentrations greater than 2,000 mg/L show a strong linear regression. It is possible that the low chloride samples are affected by dilution.

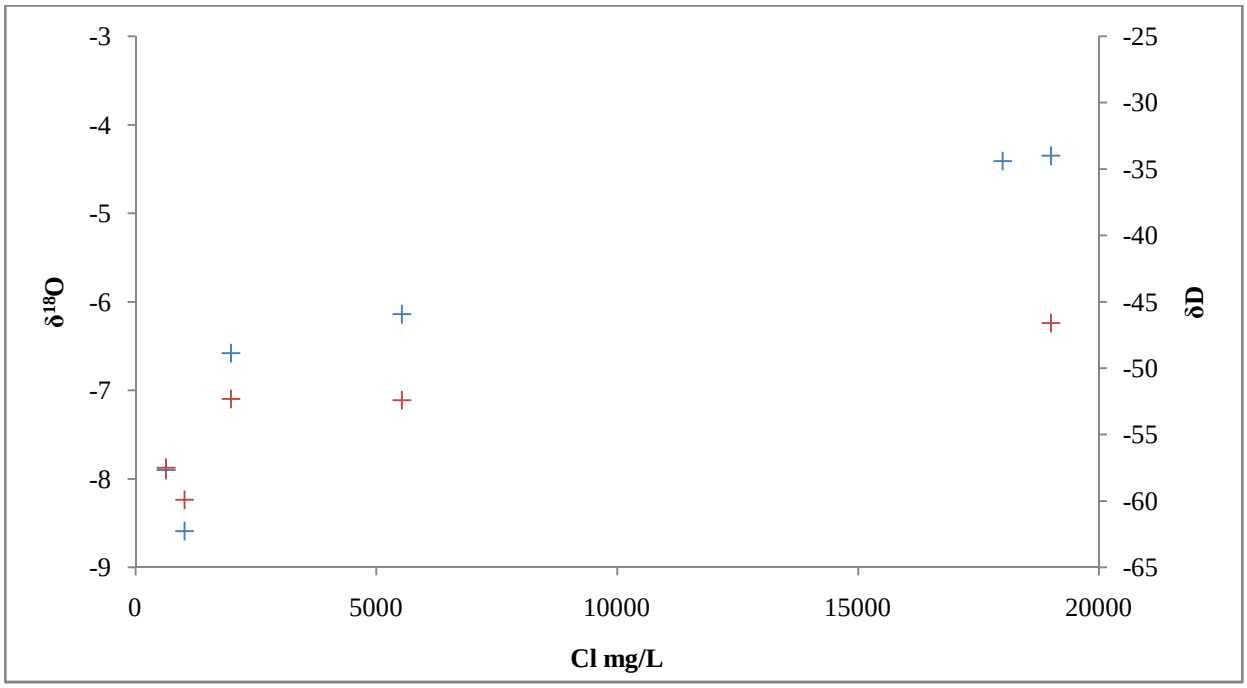


Figure 4.6: $\delta^{18}O$ and δD versus Cl for saline well samples in the Wairau Valley.

The regression line could indicate a potential mixing between two water types. Assuming mixing is occuring, one end member must be Wairau River water as the end of the regression line with the lowest $\delta^{18}O$ and δD ratios is within error (±2 sigma) of average Wairau River values. There are three potential sources for the second end member, these are; originating from seawater which has undergone subsequent ^{18}O enrichment through isotope exchange reactions with rock, seawater enriched through evaporative concentration, or a water of metamorphic origins.

Metamorphic waters are enriched in ^{18}O relative to meteoric waters (Figure 4.1). They can be derived from upward migration of deep crustal fluids or from deep circulating meteoric water which has undergone subsequent ^{18}O enrichment and comes into equilibrium with the host rock. The saline regression line (Figure 4.10) includes all saline samples, the R^2 value suggests there is little derivation from this regression. The slope of the line could potentially represent mixing with an end member water which is in equilibrium with metamorphic rocks (Figure 4.1), however, further analysis of the hydrochemical nature of the saline water is needed to fully evaluate the viability of this alternate interpretation.

4.4.2 $\delta^{13}C$

The $\delta^{13}C$ data was sampled by the Marlborough District Council and sent to GNS. Samples were sent from GNS to Woods Hole Laboratory in Massachusetts for analysis. Appendix 4.2 contains the analysis from Woods Hole. Table 4.2 contains the $\delta^{13}C$ sample for O28w/0219.

Table 4.2: $\delta^{13}C$ for Wairau Valley saline groundwater

Well Number	$\delta^{13}C$ ‰
O28w/0219	-26

The $\delta^{13}C$ analysis on the saline water at O28w/0219 is very interesting and is significant in understanding the origin of the groundwater. The $\delta^{13}C$ value of -26‰ suggest that seawater is not likely related to the saline water in the Wairau Valley. A $\delta^{13}C$ signature much closer to zero would be expected for a seawater source. $\delta^{13}C$ values seen in O28w/0219 are indicative of terrestrial vegetation. A paper by Templeton, *et al.* (1998) suggests that metamorphic fluids migrating up the Alpine fault have $\delta^{13}C$ values between -3‰ to -9‰. The same paper also found calcite precipitated in Pleistocene gravels with associated immature organics from basinal fluids with $\delta^{13}C$ values of approximately -23‰. If the Wairau Valley saline water comprised of a mix between seawater and terrestrial derived meteoric water it, well O28w/0219 should have a significantly higher $\delta^{13}C$ value due to chloride concentrations in the same well containing chloride concentrations close to seawater.

4.5 Age of the Wairau Valley Saline Water

4.5.1 O28w/0219: Tritium, SF6, CFC age Dating

Water samples from O28w/0219 along with shallow test well O28w/0220 were collected by the Marlborough District Council and analysed by GNS labs for initial investigations in the age of the saline water below the Wairau Valley aquifer. These data complement earlier tritium samples collected by Taylor (2003) and the Marlborough District Council of other saline wells in the study area. Appendix 4.3 describes the sampling methods of Tritium, SF6, and CFC sampling.

Table 4.3 Contain the Tritium, SF6, CFC-11, CFC-12 and methane concentrations for deep well O28w/0219 and test well O28w/0220 which screens within the Wairau Valley Aquifer approximately 15 m north of O28w/0219.

Table 4.3: Tritium, SF6, CFC-11, CFC-12, and methane concentrations for 2 O28w/0219 samples and test well O28w/0220.

Well Number	Depth (m)	Sampling Date	TR	sig TR	SF6	CFC-11 pptv	CFC-12	CH_4 µmol/L
O28w/0220	12	14/12/2006	1.91	0.05	5.25	166	442	-
O28w/0219	50	9/5/2007	0.014	0.021	-	-	-	-
O28w/0219	50	4/7/2007	0.003	0.026	1.08	1.9	29,000	873

Two tritium samples were collected, the first was sampled immediately after the well was extended to 50 m, and the second was two months later and required Marlborough District Council pumping equipment. Tritium is completely absent from both samples indicating that the water predates 1950. For a sample that contains no tritium both SF6 and CFC's are high and are considered the result of contamination during sampling. It was not possible to purge the well of three volumes of water because it ran dry (P. Davidson, pers. Comm. 2008) consequently air contamination has probably influenced the sample. It is likely that CFC's in the deep groundwater are degraded as the water is in a highly reducing environment represented by the high concentrations of iron, manganese (Table 5.1), and methane (Table 4.3). CFC-11 show no air contamination which is though to be a result of the type of bottle used to collect the sample which is smaller for CFC-11 samples. CFC-12 sample are extremely high and could be contaminated from residual drilling fluids in the well (MDC Groundwater Group, 2007). The results from the SF_6 and CFC help constrain the age when compared with tritium are of little significance due to the lack of tritium present.

Samples collected by Taylor (2003) from saline wells O28w/0122 and O28w/0134 (Table 4.4) suggest the saline water consists of a mix of old water pre 1952 and younger water post 1952. It is interesting that O28w/0134 has some tritium present at depths very close to O28w/0219 on the lower terrace, however, this may be due to the relative distances from the Wairau Fault which is thought to be acting as a conduit for Wairau River water.

Table 4.4: Tritium values for selected wells and rivers in the Wairau Valley

Sample Source	Well Depth (m)	Sampling Date	Tritium (TU)	sig TR
O28w/0122	10.55	26/6/2002	0.0551	0.028
O28w/0134	47.2	26/6/2002	0.0559	0.028
Wairau River	-	25/06/2002	2.39	0.05

4.5.2 O28w/0219: $\delta^{14}C$

A water sample at O28w/0219 was collected for ^{14}C analysis to determine the age of the saline water after tritium samples indicated the water was pre 1950. The sample was collected by the Marlborough District Council and sent to GNS. GNS sent the sample to Woods Hole Laboratory, Massachusetts to measure the percent modern carbon, and $\Delta^{14}C$. An age for the saline sample was not given due to the variation in the chemical constituents and only one ^{14}C sample (P. Davidson, pers. Comm. 2008).

Table 4.5 contains the data from the age analysis of O28w/0219, Appendix 4.2 contains the actual data from Woods Hole.

Table 4.5: Carbon14 data for O28w/0219, age is an estimate from the half-life and standard radioactive decay equation

Well Number	Percent Modern Carbon (pmc)	Estimated Age of sample (Years B.P.)
O28w/0219	4.24 ± 0.07	25,000

The age estimate is based on the half-life and standard radioactive decay equation. Using this half life to determine the age may not be accurate for groundwater samples because certain reactions can introduce ^{12}C to the groundwater which will give an apparent older age than actual age. Geochemical modelling is used to overcome this problem, however, this is something that would have to be completed by the laboratory that analysed the sample. Despite this issue the age of 25,000 years B.P. is considered a reasonable estimate for the age of the saline water. Due to the very low percent modern carbon value the age calculated is probably close to the

minimum age, however, the value could represent a mix between water significantly older than minimum $\delta^{14}C$ age with younger water. Only a small proportion of young water is required to give a realistic age for a mix water that is significantly older the minimum age range.

6.3 Paleo-physiographic setting of the Wairau Valley

The paleo-physiographic setting of the Wairau Valley is based on the age calculated from the ^{14}C of 25,000 years B.P. Due to the high uncertainty of this age the physiographic setting described below relates to the Last Glacial Maximim (LGM) in general. However, similar conditions would have persisted around this time. This setting is considered to be representative of the conditions at the time when the saline water in the Wairau Valley was last at the surface.

Between approximately 34,000 years and 16,000 years B.P. was a major cold period (Suggate & Almond, 2005). Ice volumes reached a maximum at 30,000 years B.P. and remained constant until approximately 19,000 years B.P. (Lambeck *et al*, 2002). Relative sea levels during this time were approximately 120-130 m lower than the present day (Lambeck & Chappell, 2001; Lambeck *et al*, 2002). Low sea levels peaked approximately 21,000-18,000 years B.P. The study area in the Wairau Valley is 170 m above present sea level, therefore, 25,000 years ago sea level would have been between 250-300 m lower than the present location of the saline water. Eden (1983) suggests between 25,000-19,000 year B.P. river aggradation and high loess accumulation resulted from low loess weathering rates in a semi-arid climate, which probably had frequent droughts. Between 70,000-19,000 years B.P. aggradation in the Wairau Valley deposited the Speargrass Gravels, which are thought to fill the valley. A river which has an aggradational depositional setting would regularly avulse across the rivers flood plain as it carried the bed load out to sea. Therefore the flood plain during this time was likely to be a very active environment which may have limited the type of vegetation. A paper by Almond *et al*., (2006) dated the age of pedogenic carbon on Banks Peninsula at 22,288-22,742 calculated years B.P. The significance of this is that soil carbonates only develop in very arid conditions. Conditions in the Wairau Valley would probably be similar to Canterbury.

During the LGM, the topographic relief around the Wairau Valley would be similar to the present day (J. Bradshaw pers. comm., 2008). Based on the recurrence interval (1,150 –

1,400 years B.P.) and single event displacement (5-7 m) data given in Zachariasen *et al.* (2006) there has been between 90-154 m of lateral offset along the Wairau Fault in the last 25,000 years.

The average annual temperature during the LGM was probably between 2.5-5^{o}C cooler than present with significant temperature oscillation and seasonal variation during this time.It is generally accepted that precipitation was lower during the LGM and generally consisted of drier conditions (Marra *et al*., 2004; Otto-Bliesner *et al*., 2006; Drost *et al*., 2007), however, regional variations dominated. The westerly wind dominated the mid latitudes in the Southern Hemisphere during the LGM (Drost *et al*., 2007). The Wairau Valley would have been well protected from westerly fronts by the Richmond Ranges as it is today. The climate in New Zealand on a local scale is largely controlled by the topographic influence on large scale circulation (Drost *et al*., 2007). This is particularly relevant in the Wairau Valley.

4.6 Chapter Summary

Saline waters in the Wairau Valley study area are clearly related. The regression line fits within the slope characteristics of kinetic fractionation by evaporation, chloride does show positive enrichment relative to $\delta^{18}O$ values, and however, it is complicated by the non-linear fit between $\delta^{18}O$ and Cl which is potentially the result of mixing between two water types. If mixing of two end-member waters is used to explain the regression line one end-member is unequivocally meteoric water of Wairau River origins, the other end-member is potentially highly saline brine of seawater origin enriched in $\delta^{18}O$, or metamorphic water which has migrated upward along the Wairau Fault. The $\delta^{13}C$ value of -26‰ for the sample at O28w/0219 suggests that the saline water is probably not seawater in origin but derived from a terrestrial setting. More $\delta^{13}C$ samples would potentially define a mixing line between two water types, however mixing is unlikely due to the highest chloride concentrations also occurring in well O28w/0219. Tritium, SF_6, CFC-11, and CFC-12 analysis indicate the saline water in O28w/0219 at 50 m depth predates 1950s recharge as it contained almost no tritium, SF6 and CFC data was inconclusive and likely contaminated during sampling, however, due to the lack of tritium this is no considered relevant. The ^{14}C sample collected contained extremely low percent modern carbon value and an estimated age is given at 25,000 years B.P., however, due to the inconsistent chemistry and only one sample at present it is difficult to constrain the age of the water further. Due to the very low percent modern carbon value, the age of 25,000 years B.P. is probably close to the minimum age

of the saline water here, however it is possible that significantly older water has mixed with younger water which is in the range of ^{14}C dating and probably less than 25,000 years B.P.

CHAPTER FIVE

GROUNDWATER CHEMISTRY

5.1 Introduction

One of the primary objectives of this study is to identify the source of the high salinity in the deep Wairau Valley water. This chapter analyses the hydrochemistry of the saline water, with the focus primarily on O28w/0219 as this is well with the highest known concentrations of dissolved solids in the Wairau Valley. Figure 5.1 shows the locations of selected wells and stream sample sites in the study area.

The nature of the saline groundwater has significant implications for the groundwater resource of the Wairau Valley and it is critical to understand the chemistry to identify the origins of the saline groundwater.

Geochemical techniques used in this chapter include facies identification of the three major water types in the field area (Southern Hills, Wairau River and Deep Saline), analysis of individual ion concentrations to attempt to identify their source. Appendix 5.1 contains the chemical data for all wells and steams in the study area.

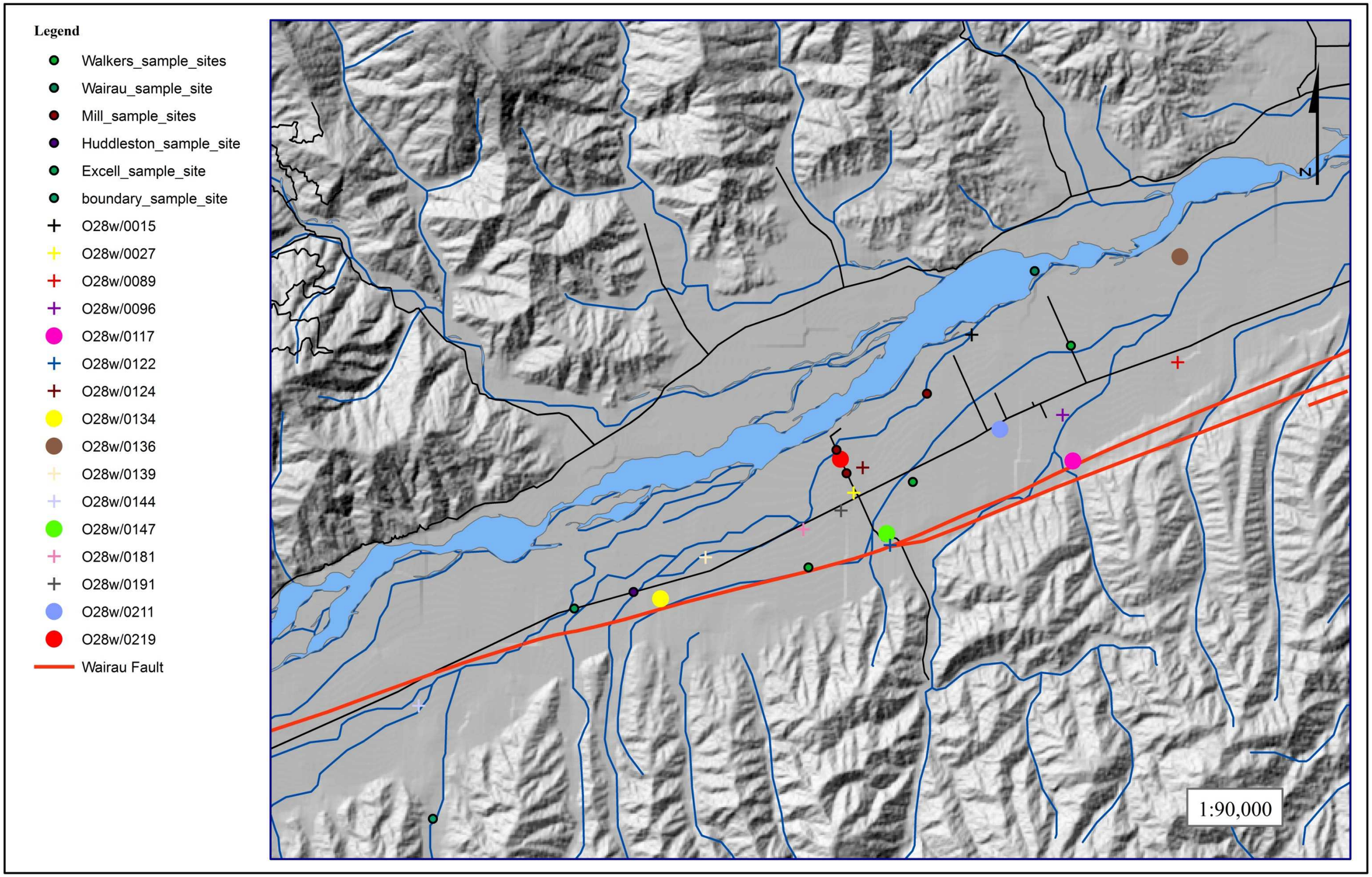


Figure 5.1: Location of well and stream samples in the Wairau Valley study area. Crosses represent freshwater wells, large circles represent saline wells, and small circles represent stream sample sites.

5.2 Major Ion Evolution Sequence

A paper by Chebotarev (1955) showed that as groundwater moves from the surface to depth where groundwater is generally older and flow is very low, the chemical composition of the groundwater will increase in total dissolved solids (TDS) and chemically move toward chloride type. Variables that control the anion-evolution sequence (Figure 5.2) are the availability of particular minerals and the solubility of the minerals present.

Groundwater Flow path →

$$HCO_3^- \rightarrow HCO_3^- + SO_4^{2-} \rightarrow SO_4^{2-} + HCO_3^- \rightarrow SO_4^{2-} + Cl^- \rightarrow Cl^- + SO_4^{2-} \rightarrow Cl^-$$

Age of the Groundwater →

Figure 5.2: The anion evolution sequence of natural groundwaters, which is largely controlled by the length of flow path and age of the groundwater (Chebotarev, 1955).

The bicarbonate concentrations of groundwater are generally developed within the soil zone as a result of the presence of atmospheric CO_2 and from calcite or dolomite dissolution. Calcite and dolomite are only moderately soluble except where CO_2 charged ground water is present Calcite or dolomite is often present within sedimentary basins, as a result bicarbonate type water is most commonly found in recharge areas (Freeze and Cherry, 1979).

Sulphate bearing minerals (for example Gypsum $CaSO_4.2H_2O$, and Anhydrite $CaSO_4$) are generally much more soluble than calcite and dolomite. If enough gypsum and calcite or dolomite is present to reach equilibrium the water will become sulphate + bicarbonate dominated brackish water in a relatively short period of time. The groundwater will be unable to evolve until more soluble minerals are present or evaporation occurs. It is rare to find gypsum and anhydrite in anything greater than trace amounts within a sedimentary basin. Over an extended period of time previous groundwater flushing can entirely remove these more soluble minerals from the active-flow zones, although the length of time required often precludes this from occurring as continual geological processes, for example sedimentation and glacialtion, refresh the groundwater system (Freeze and Cherry, 1979).

Where groundwater comes in contact with highly soluble chloride minerals (for example halite) it will evolve past sulphate dominated to chloride rich brine which is very high in TDS. Chloride

minerals are greater than an order of magnitude more soluble than both bicarbonate and sulphate minerals, therefore if present in a groundwater system will be quickly dissolved into the groundwater. These waters are generally found at depth within the basin, but sometimes in shallower systems.

Halite, an evaporite, is often deposited in closed or restricted marine basins millions of years ago. If halite is present the groundwater will very quickly move into the chloride phase. Other chloride minerals, which are not found as evaporate beds, are very rare in sedimentary basins. It is thought chloride type waters where halite dissolution is not the source of the chloride ions are very old and have travelled long distances through geological units with only trace amounts of chloride. The uptake of chloride by the flowing groundwater is largely controlled by diffusion from the matrix of the porous media to the larger pores and fractures where significant groundwater flow is taking place. Diffusion is a very slow process therefore the evolution of the groundwater from sulphate + chloride to chloride type water is usually very gradual (Freeze and Cherry, 1979).

5.3 Wairau Valley Saline Water Chemistry

Wells within the field area with total dissolved solids greater than 1000 mg/L are consider saline in this study. This value is significantly higher than the background concentrations from Southern Hills runoff and Wairau River water. The highest concentrations are found in O28w/0219 (31,000 mg/L). O28w/0134 has the second highest dissolved solids concentrations at approximately 9,000 mg/L. The samples from O28w/0219 are clearly less diluted and are probably more representative of the initial source of the high dissolved solids. Table 5.1 contains the ion composition of three samples from O28w/0219, along with seawater as reference. Three samples do not have an ion balance below 5%, two of these are relatively close to the 5% threshold, one sample from O28w/0134 however, has an error of 13% and is poor analysis. Figure 5.3 shows selected ions verses chloride along with the seawater value and evaporation trend to allow for comparison. This section discusses the concentrations of important ions present in the saline water and attempts to define the source of the constituents where possible.

Table 5.1: Chemistry of selected well and river samples in the Wairau Valley Field area.

	O28w/0117		O28w/0134		O28w/0134		O28w/0134		O28w/0136		O28w/0147		O28w/0147		O28w/0211		O28w/0219		O28w/0219		O28w/0219		O28w/0220		Wairau		Seawater	
Samplle ID	20020507		20020502		20030031		20050589		20020512		20074973		20020505		20073693		20072294		20073616		20080603		20067752		20067754		-	
	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l	Mg/L	Meq/l
Well Depth (m)	10.68		47.2		47.2		47.2		35		shallow		shallow		13.9		50.48		50.48		50.48		12		-		-	
pH	7.5	-	7.4	-	6.8	-	7.34	-	7.8	-	6.9	-	7.3	-	-	-	6.831	-	8.26	-	5.7	-	7.2	-	7.7	-	-	-
TºC	14.2		15.1		-		12.2		13.8		18.3		14.8		-		15.3		13.6		14.6		12.8		12.9		-	
Na^{+}	273	11.88	2680	116.6	2400	104.398	2700	117.4	530	23.05	1030	44.80	1220	53.07	370	16.09	8300	361.0	8300	361.0	7900	343.6	15	0.652	5.4	0.235	10760	468.0
K^{+}	-	-	16.5	0.422	16.7	0.427	17	0.43	4.07	0.104	20	0.512	11.6	0.297	2.1	0.054	19	0.486	13	0.332	19	0.486	1	0.026	0.6	0.015	399	10.21
Ca^{2+}	107	5.340	530	26.45	467	23.30	520	25.95	81.6	4.072	140	6.986	162	8.084	50	2.495	3200	159.7	3400	169.7	2900	144.7	10	0.499	6.6	0.329	411	20.51
Mg^{2+}	31.2	2.567	68.4	5.628	83.3	6.855	64	5.27	7	0.576	42	3.456	54.7	4.501	7.9	0.650	47	3.868	77	6.336	61	5.020	2.4	0.197	1.5	0.123	1290	106.2
Fe^{2+}	1.23	0.044	11.8	0.423	15.9	0.569	4.7	0.17	1.03	0.037	5.4	0.193	6.67	0.239	0.26	0.009	6	0.215	55	1.970	52	1.862	0.006	0.0002	0.033	0.001	2	0.072
Cl^{-}	636	17.94	5530	156.0	6210	175.161	5300	149.5	1020	28.77	1980	55.85	2580	72.77	710	20.03	19000	535.9	20000	564.1	18000	507.7	23	0.649	6	0.169	19350	545.8
SO_4^{2-}	<0.2	-	0.2	0.004	21	0.437	0.56	0.01	1.1	0.023	0.5	0.010	<0.2	-	4.1	0.085	0.15	0.003	1.8	0.037	0.85	0.018	5	0.104	2.6	0.054	2710	56.42
HCO_3^{-}	197.64	3.239	206.2	3.379	147.6	2.419	170.8	2.80	85.4	1.400	-	-	285.5	4.679	150	2.458	84	1.377	4.4	0.072	3.8	0.062	40	0.656	34.16	0.560	142	2.327
Br^{-}	-	-	-	-	11.5	0.144	-	-	-	-	-	-	-	-	1.1	0.014	28	0.350	33	0.413	45	0.563	<0.15	-	<0.15	-	67	0.839
F^{-}	<0.05	-	<0.05	-	<0.05	-	-	-	<0.05	-	-	-	<0.05	-	0.091	0.005	0.05		0.05	-	0.45	0.024	0.088	0.005	0.056	0.003	1.3	0.068
SiO_2	32	0.533	8	0.133	-	-	9.1	0.15	11	0.183	-	-	25	0.416	17	0.283	14	0.233	31	0.516	0.5	0.008	15	0.250	9	0.150	0.5-10	-
Mn^{2+}	3.78	0.138	2.4	0.087	1.35	0.049	1.2	0.04	0.289	0.011	3.7	0.135	7.14	0.260	0.32	0.012	5.8	0.211	8	0.291	3.4	0.124	0.002	0.0001	0.003	0.000	0.0002	-
As^{3-}	0.008	0.000	<0.01	-	<0.005	-	<0.002	-	<0.001	-	-	-	<0.01	-	<0.002	-	0.023	0.001	0.001	0.000	0.001	0.000	<0.001	-	<0.001	-	0.003	-
B	0.7	0.065	13.2	1.221	10.2	0.943	13	1.20	4.4	0.407	-	-	26.4	2.442	4.7	0.435	18	1.665	24	2.220	23	2.127	0.07	0.006	-	0.000	4.5	0.416
$N\text{-}NH_3$	0.38	0.011	1.4	-	1.5	-	1.3	-	0.17	-	0.24	0.007	2	0.056	0.26	-	5.8	0.164	4.9	0.138	5.8	0.164	<0.005	-	0.005	-	-	-
$N\text{-}NO_3$	<0.05		<0.05	-	<0.05	-	0.003	-	<0.05	-	0.011	0.0001	<0.05		0.32	-	0.004	0.000	<0.02		0.1	0.001	1.7	-	0.22	-	-	-
Cations	-	19.83	-	149.5	-	135.6	-	149.3	-	27.84	-	55.95	-	66.19	-	19.30	-	525.3	-	539.3	-	495.7	-	1.375	-	0.704	-	605.0
Anions	-	21.19	-	159.5	-	178.2	-	152.3	-	30.20	-	55.99	-	77.71	-	22.60	-	537.9	-	564.9	-	508.5	-	1.413	-	0.786	-	605.4
Error%	-	-3.324	-	-3.222	-	-13.595	-	-1.022	-	-4.066	-	-0.038	-	-8.006	-	-7.870	-	-1.182	-	-2.317	-	-1.272	-	-1.375	-	-5.507	-	-0.038
TDS	1282.94	-	9068.08	-	9386.07	-	8801.66	-	1746.06	-	3221.85	-	4381	-	1318.15		30727.8	-	31952.2		29014.9	-	113.266	-	66.177	-	35136.8	-

Colours represent the source water for the sample, pink = saline wells, green = Southern Hills derived water, Blue = Wairau River water, and Orange = the composition of seawater (Seawater chemistry from Drever, 1997).

To calculate the mass balance error equation [5.1] is used with an acceptable error percentage of ± 5% (Hounslow, 1995)

$$\text{Error } \% = \frac{(\text{Tt}+) - (\text{Tt}-)}{(\text{Tt}+) + (\text{Tt}-)} \times 100 \qquad [5.1]$$

Yellow box highlights poor mass balance.

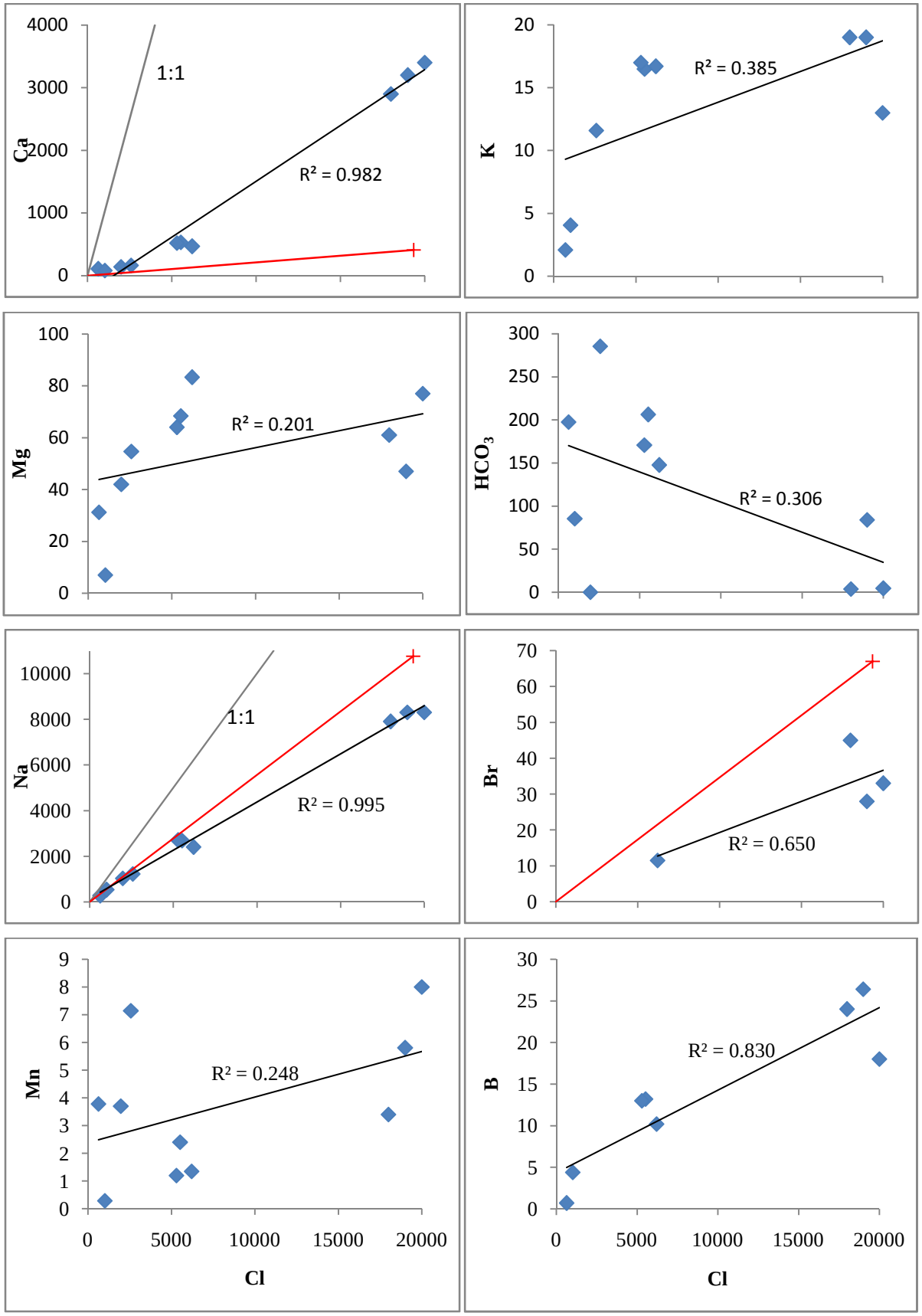


Figure 5.3: Selected ion concentration versus chloride, values in mg/L, red line represents evaporative trend of seawater (red cross).

5.3.1 Sodium

Common sources of sodium in groundwater include silicate weathering and the breakdown of feldspars plagioclase, albilte ($NaAlSi_3O_8$) and to a lesser extent nephelene ($NaAlSiO_4$). Na and Ca species of feldspar are much more susceptible to weathering than K feldspar with the products being Na or Ca along with silica to solution and clay (usually kaolinite). Below is the formula for weathering albite forming kaolinite and soluble Na and SiO_2:

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O = Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2Na^+ \quad [5.1]$$

(Albite) (Kaolinite)

In the majority of natural waters cation exchange between clays (commonly montmorillonite due to it high cation exchange capacity) can lead to sodium enrichment at the expense of either calcium or magnesium, the equation for cation exchange is (Fitts, 2002):

$$2(\equiv XNa) + Ca^{2+} \leftrightarrow \equiv XCa + 2Na^+ \quad [5.2]$$

$\equiv X$ represents the cation exchanging solid, in the situation of Na^+ and Ca^{2+}, two sodium ions are required to replace Calcium. Sodium sinks include halite formation and reverse ion exchange, however, Rosen (2001) states this process is not common in New Zealand waters. Generally ions that consist of a bivalent charge (for example Mg^{2+} and Ca^{2+}) more easily displace monovalent cations (for example Na^+), therefore once sodium is in solution is not easily removed (Fitts, 2002).

Where significantly high quantities are present seawater, connate water, halite dissolution, hot springs or brines often are the source. However, over long residence times, interaction with rock can produce high levels through weathering albite feldspars.

Sodium concentrations are relatively consistent for the three samples at O28w/0219, the slight variation correlates well with chloride concentrations suggesting they share a common origin (Figure 5.3). High sodium concentrations with high chloride concentrations are often the result of seawater influence via connate, evaporite, or seawater intrusion, however, the total chemistry and geographic location suggests a more complicated history.

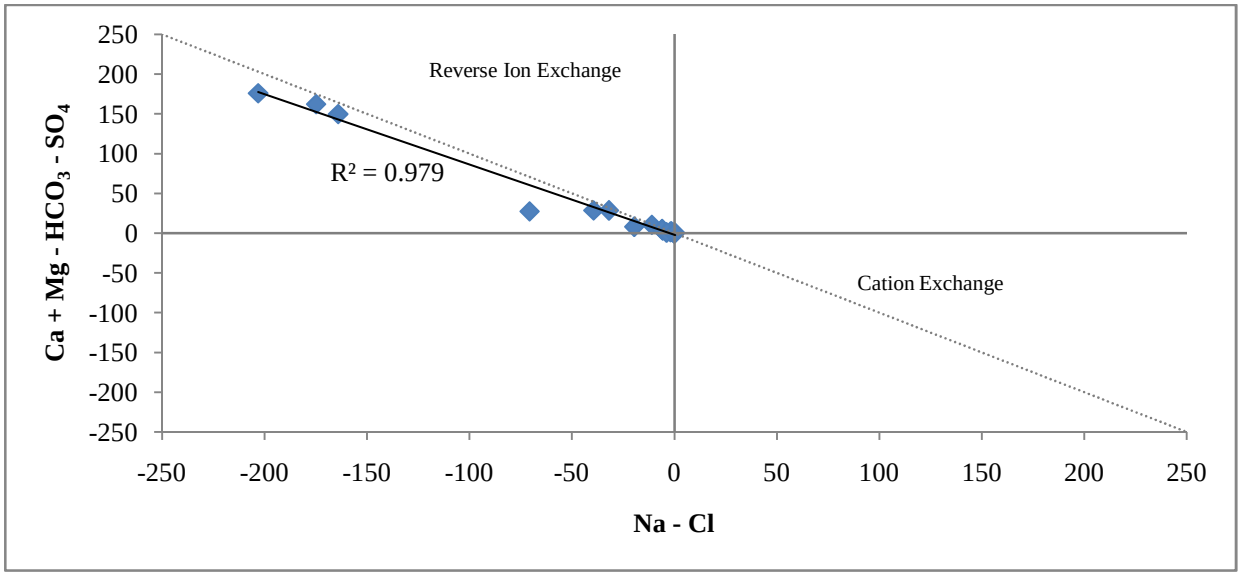


Figure 5.4: $Ca^{2+} + Mg^{2+} – HCO_3 – SO_4^{2-}$ versus $Na^- – Cl^-$ diagram of Wairau Valley saline water suggesting reverse ion exchange from groundwater with the original source composition from dissolution of halite.

Figure 5.4 suggests reverse ion exchange has influenced the chemistry of the Wairau Valley saline groundwater, assuming halite dissolution is the initial source of the high salinity. The Wairau Valley saline samples plot very close to the 1:1 line delineating ion exchange reactions. Groundwaters not affected by cation exchange will have values at zero on both the x-axis and y-axis. Cation exchange generally removes calcium from the fluid and releases sodium, therefore, sodium is enriched relative to chloride and depleted in calcium relative to bicarbonate and sulphate. Reverse ion exchange is a process that removes sodium from the fluid exchanging with calcium resulting in a groundwater enriched in calcium relative to bicarbonate and depleted in sodium. In the case of halite dissolution sodium would be significantly less than chloride (Morgan and Jankowiski, 2004).

For cation exchange to take place, clay with high cation exchange capacity (CEC) is required. XRD analysis of the clay in O28w/0219, suggests the predominant clay present is Kaolinite, which forms from the breakdown of Na-feldspars. No other clay was identified in the samples analysed in O28w/0219 which were collected at varying depths during extension of the well. Kaolinite has a very low CEC of 3-15 meq per 100 g (Carroll, 1959) and no calcium is present in its lattice. For reverse cation exchange to account for the sodium concentrations it must have taken place prior to entering the Wairau Valley. It may be possible that the sodium concentrations are entirely the result of the breakdown of Na-feldspars over an extended

residence time, however, due to the very good relationship between sodium and chloride it is more likely that they are derived from a single source.

5.3.2 Calcium

Calcium is an important element of many igneous-rock minerals; for example pyroxene (diopside, $CaMgSi_2O_6$), amphibole and feldspars (anothite, $CaAl_2Si_2O_8$) an end member of the plagioclase group) along with other silicate minerals are produced in metamorphism. However, because weathering of many igneous and metamorphic rock minerals is a slow process, concentrations would remain low. Because plagioclase feldspar generally lies on a continuum between sodium and calcium, weathering would produce both calcium and sodium ions along with soluble silica. Carbonates are the most abundant source for calcium in sedimentary rocks. Limestone which is predominately calcite and dolomite, has a Ca/Mg_{Molar} ratio approaching 1. Sulphates, gypsum ($CaSO_4.2H_2O$), and anhydrite ($CaSO_4$) are important sources of calcium in natural waters and are often related to halite. Dissolution of these minerals would result in high levels of sulphate in the water. Over a relatively long period of time, if the pH is high enough calcium carbonate will precipitate from solution. This often occurs where geothermal water has migrated up fractures in fault zones, often carrying other minerals such as metals in solution.

Calcium concentrations are elevated in the saline waters in the Wairau Valley relative to Wairau River and Southern Hills waters. Calcium verse chloride plots show a very good linear correlation (Figure 5.3) suggesting they are related. Figure 5.5 shows that in the Wairau Valley saline water, calcium is enriched relative to bicarbonate suggesting that calcite dissolution or silicate weathering is not the source of the calcium in these waters. Reverse cation exchange could explain both the lower sodium and high calcium in the saline waters.

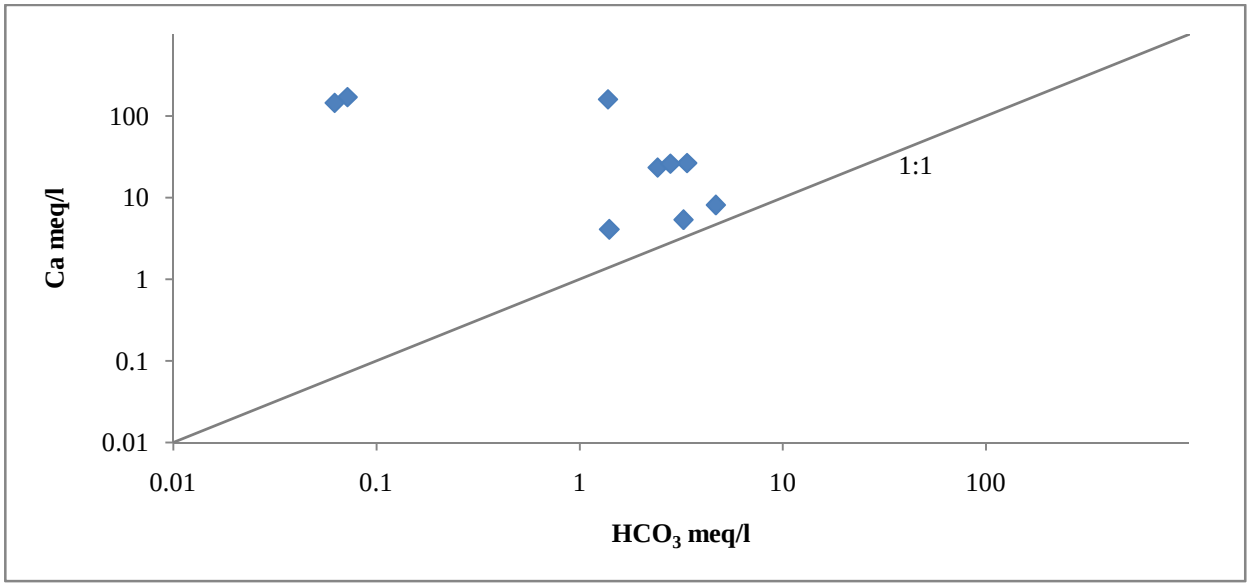


Figure 5.5: Ca versus HCO_3 indicates the source of the calcium in natural waters. Calcite dissolution would plot along the 1:1 line, silicate weathering would plot close to or below the 1:1 line. Waters where calcium plots above the 1:1 line suggests another source of calcium, which is the case here.

5.3.3 Potassium

Compared to sodium, potassium is slightly less abundant in igneous rocks, whereas, in sedimentary rocks potassium is found at much higher concentrations. Potassium is more difficult to weather from minerals than sodium (i.e. K-feldspar is more resistive to weathering than Na-feldspar) and is also more easily reincorporated into weathering products through cation exchange. For these reasons potassium is generally found in much lower levels than sodium in natural waters. Orthoclase and microcline are two common potassium bearing minerals which break down very slowly in water. A source for high concentration of potassium is generally seawater intrusion, sea spray, connate brines or dissolution of evaporite deposits. Seawater contains 399 mg/L potassium (Drever, 1997). Common sinks include the formation of evaporite deposits, conversion of kaolinite to illite, and cation exchange. Potassium is also preferred over sodium in sorption (Fitts, 2002; Hanor, 1983).

Potassium concentrations show no correlation with chloride (Figure 5.3) and are significantly lower than sodium and calcium concentrations in O28w/0219, and much lower than seawater concentrations. Due to its chemical nature potassium is preferentially removed from a fluid over sodium, therefore, it is possible that concentrations have been significantly higher in the past indicating seawater as the initial source of the salinity. However, a more simple explanation is

dissolution halite. Potassium salts (for example Sylvite KCl) is more soluble than halite and will also precipitate out after halite during evaporation, therefore, high sodium and chloride concentrations with very low potassium can often reflect dissolution of halite.

5.3.4 Magnesium

Dolomite is the most common natural source of large volumes of Mg ($CaMg(CO_3)_2$) where it will generally be present in similar concentrations to Ca. It is also associated with ferromagnesian silicates in igneous rocks, for example olivine ($(Mg,Fe)_2SiO_4$), pyroxene (diopside, $CaMgSi_2O_6$), amphibole ($NaCa_2(Mg,Fe,Al)Si_8O_{22}(OH)_2$), and dark micas ($K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$). Sinks include cation exchange with montmorillonite clays, and precipitation of magnesium chlorite from saline waters.

Magnesium concentrations are elevated with respect to Wairau River and South Hills waters, but are significantly lower than calcium in samples from O28w/0219. (The seawater magnesium concentration is 1290 mg/L), which is significantly higher than the saline water in the Wairau Valley. Reduction of fluid concentrations could occur through cation exchange, however magnesium has weak sorption compared to calcium, potassium, or sodium (Fitts, 2002). Due to the vey old age of the saline water in the Wairau Valley magnesium concentrations are probably derived from the Torlesse, Mg verse Cl diagram (Figure 5.3) indicates no correlation between the two ions indicating that magnesium values are not related to evaporation.

5.3.5 Iron

Iron (Fe) generally only occurs in any significant concentrations in moderately reduced waters (1 – 10 Mg/L), as ferrous iron (Fe^{2+}). If H_2S is present in highly reducing waters ferrous iron is precipitated as a sulfide, pyrite, or marcasite.

Igneous minerals such as pyroxenes, amphiboles, biotite, magnetite and olivine (Fayalite) contain some Fe. In these rocks it is most commonly in ferric form (Fe^{3+}). Ferrous and ferric iron is widespread in sedimentary rocks. Iron concentration in groundwater is primarily controlled by the dissolved oxygen concentration (T. Horton, pers. comm., 2008) which is controlled by the temperature of the water, where cold water holds less dissolved oxygen than warm water.

Iron concentrations in O28w/0219 is high in one of the samples (6 mg/L) and extremely high in the other two (52 mg/L and 55 mg/L). All three samples are similar in temperature range and do not show any significant variation at different times of the year. Due to the low flow at 50 m depth seasonal variation is not considered a significant factor in the difference in the iron concentrations. The dissolved oxygen concentration is not known for each sample, however, the water in O28w/0219 has been identified as reducing due to high concentrations of methane, iron, manganese, and very low concentrations of sulphate. It is possible that the high iron levels in two of the samples are the result of contamination during sample collection. More samples need to be collected in the future it is difficult to accurately understand the nature of the iron concentration in O28w/0219.

5.3.6 Chloride and Bromide

Three-quarters of the chloride (Cl) in the upper 16 km of the earths crust is thought to be in the oceans. Chloride generally occurs in natural waters and in rock at lower concentrations than any of the other major ions in natural water. Sodalite and apatite are two chloride bearing igneous minerals, but chloride can also occur in residual pore water or within crystals in granite. Chloride can replace hydroxide in biotite and hornblende, however, igneous rocks generally cannot provide high concentrations of chloride to natural waters.

Sedimentary rocks are a much more important source of chloride, especially evaporites. Any deposit laid down in the ocean or in a closed drainage basin that has not been completely leached will contain soluble salts. Any porous rock that has been submerged will also contain soluble salts. Fine grained marine shales can retain chloride for a very long time. Deeply buried marine shales have an average chloride content of 1,466 mg/L (Billings & Williams, 1966) This differs from most surface shales which have had most of their salts leached. In all of these chloride is usually accompanied by sodium and bromide in either crystal form or in solution.

The geochemical characteristics of bromine and chlorine are very similar, they are both highly conservative. They most commonly occur as monovalent ions in solution, and generally occur in very low concentrations in common rock forming minerals. Both are highly soluble especially when in simple compounds and have low bio-accumulation in aqueous environments (Davis *et al*., 1998).

The major difference between the two ions is their relative concentrations in a natural environment (Davis *et al*., 1998). An example of this is in seawater where chloride is approximately 19350 mg/L and bromide only 67 mg/L (Drever, 1997). This leads to large changes in the Br/Cl ratio with only minor changes in the bromide content (Davis *et al*., 1998). The relative solubility of bromide and chloride is another important geochemical difference; bromide is much more soluble than chloride, during evaporation chloride will precipitate first as halite leaving brine enriched in bromide (Davis *et al*., 1998). Where precipitation from seawater comes to an end the residual brine will have a Cl/Br ratio of 50 and the halite approximately 9000 (McCaffery *et al.*, 1987). This can be further enriched if dissolution of the halite by fresh water and further evaporation occurs. This mechanism can lead to extremely low Br/Cl ratios. Most studies have shown little or no evidence of sorption of these ions in both field and laboratory experiments (Davis *et al*., 1998). Conversely, Wilson & Gabet (1991) report approximately 10% sorption on clays, soil and organic debris. Boggs & Adams (1992) reported between 15% and 20% sorption of dissolved bromide at pH 4.7 on Kaolinite and iron oxides, but no losses at a neutral pH.

Halite has a bromide concentration of approximately 68 mg/L, brine derived from dissolution of halite, which has a similar Cl content to seawater, would contain only 2.3 mg/L bromide or a Br/Cl ratio approximately 5.27×10^{-5} (Whittemore, 1995).

Figure 5.6 clearly suggests that all the chloride in the Wairau Valley saline water can be accounted for by sodium and calcium cations, which plot along a 1:1 line against chloride.

Taylor (2003) suggests this is due to seawater which has undergone reverse cation exchange, replacing the two sodium ions for one calcium ion in the water. Seawater plots slightly lower than 1:1 for Sodium verse chloride. Sodium verse chloride during the dissolution of halite (NaCl) plots perfectly along the 1:1 line (Figure 5.3), therefore, salinity derived from dissolution of halite which subsequently has undergone reverse cation exchange is a better fit for this data. Another way to describe this relationship is that mixing between two water types (sodium-chloride and calcium-chloride) has occurred at some point in the past history of this water (T. Horton, pers. comm., 2008). Sodium-chloride and calcium-chloride waters form through progressive salinisation of sodium bicarbonate or calcium-sulphate groundwaters.

Reverse cation exchange with a high salinity water can lead to calcium-chloride water formation by exchanging the sodium in the water with bound calcium. Where relatively young fresh waters mix with older, highly saline waters (Adams *et al*, 2001) younger waters are often high in calcium relative to other cations whereas older waters tend towards chloride type as described by (Chebotarev, 1955).

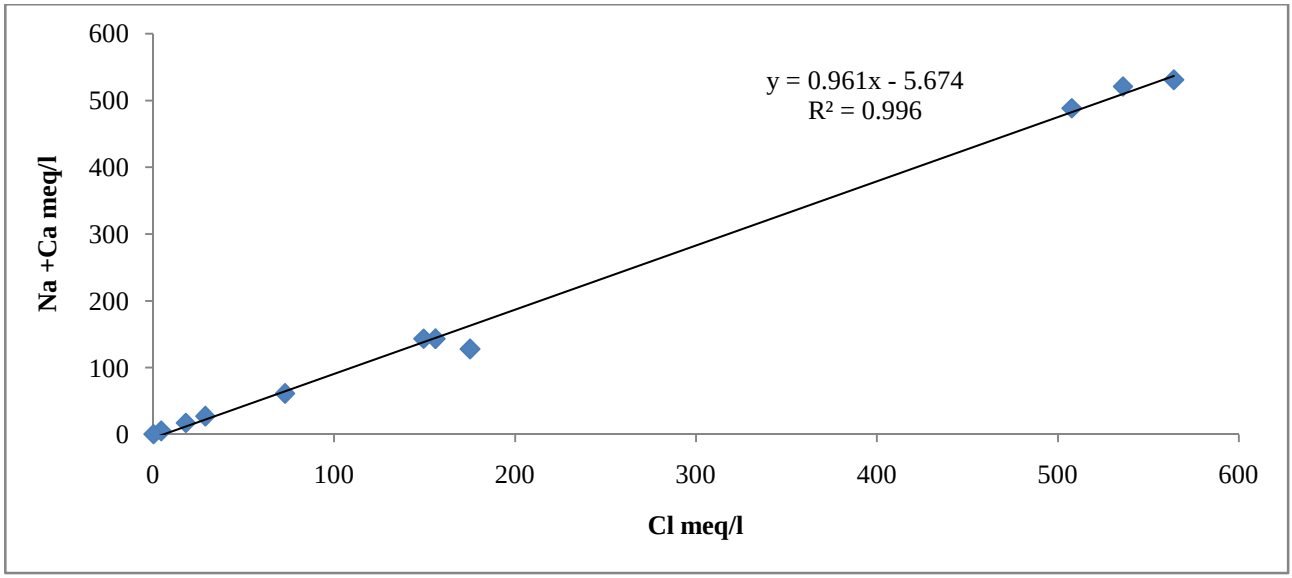


Figure 5.6: Na+Ca verse Cl diagram for saline wells in the Wairau Valley,

5.3.7 Sulphate

Sources of sulphate include pyrite, evaporites (gypsum and anhydrite), geothermal waters, and seawater. Common sinks include precipitation of evaporites, sulphate pyritization, and sulphate reduction. Sulphate reduction occurs over extended time periods under anaerobic conditions whereby sulphate-reducing prokaryotes reduce sulphate to hydrogen sulphide by using organic compounds or hydrogen as an electron donor (Hounslow, 1995):

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \qquad [5.3]$$

Hydrogen sulphide precipitates metals as sulphides:

$$H_2S + M^{2+} \rightarrow MS + 2\,H^+ \qquad [5.4]$$

Where M^{2+} = metal, such as Fe^{2+}, Mn^{2+}, or Zn^{2+}

The oxidation of electron donors produces alkalinity (for example HCO_3^-) which neutralizes acidic water:

$$HCO_3^- + H^+ \rightarrow CO_2(g) + H_2O \qquad [5.5]$$

O28w/0219 samples have probably undergone sulphate reduction with only one sample greater than the measurable minimum concentration. The hydrogen sulphide concentration of the water is not accurately known. During drilling there was no hint of the characteristic “rotten egg” smell present with only a few tenths of a milligram per litre present in solution. Also unknown is the carbon dioxide levels in O28w/0219 which would be expected to be high to reduce the bicarbonate that is produced during sulphate reduction and is clearly not present in the saline water.

5.3.8 Bicarbonate

Major sources of bicarbonate in groundwaters include carbonate dissolution, sulphate reduction, or CO_2 interacting with atmospheric water. Dissolution of carbonates (calcite, aragonite, or dolomite) generally produce the highest bicarbonate concentrations in natural waters. In the case of calcite dissolution, the water will have a Ca/HCO_3 ration of close to 1. Dolomite contains high quantities of magnesium, which would be reflected by a Ca/Mg ratio near 1 (Hem, 1992). Weathering silicates (albite) will produce some bicarbonate, and in this situation silica concentrations will be comparable to bicarbonate. Waters that have undergone sulphate reduction often contain high concentrations of bicarbonate, a natural resultant of the sulphate reduction reaction (equation [5.3]). The most common sink for calcite is precipitation of calcite (Hounslow, 1995). However, equation [5.5] shows that in acidic conditions the water will be neutralised by converting bicarbonate to carbon dioxide (Hounslow, 1995).

Samples from O28w/0219 are generally very low in bicarbonate, two of the samples show between 3.5 and 4.5 mg/L and one sample 84 mg/L (Table 5.1). It is important to collect more samples to better define the bicarbonate concentration in O28w/0219, however, some conclusions can be made from the present data. For all of the saline water samples bicarbonate concentrations are highest for the well with the lowest chloride concentration (Figure 5.3). It would be expected that the high bicarbonate concentrations are from mixing between saline

water and Wairau River water, however, both Southern Hills and Wairau River water have very low bicarbonate concentrations.

5.3.9 Manganese

Manganese is generally low in natural waters. High concentrations usually suggest moderately reduced water conditions where iron concentrations are also high. Compared to iron, manganese takes a significantly longer time to precipitate out. Manganese often occurs in minerals which can substitute divalent ions, for example biotite and hornblende. Manganese carbonate will have high concentrations of manganese (Hem, 1992).

High concentrations present in all three sample from O28w/0219 suggest that the water has been subjected to anoxic conditions for a significant period of time. Manganese is present in the Torlesse Terrane and probably has a similar origin to the boron and iron in O28w/0219.

5.3.10 Fluoride

Fluoride concentrations in seawater is approximately 1.3 mg/L (Drever, 1997), which is much less than the other halogens chloride and bromide. Fresh water usually contains less than 1 mg/L of fluoride. The amount of fluoride in rocks exceeds chloride and is present in many common mineral species such as calcium fluoride (CaF_2) and apatite (Ca_5 $(PO_4)_3$ (OH^-,F^-,Cl^-)). Hornblende and some micas can contain fluoride replacing part of the hydroxide. Rocks which have high concentrations of alkali metals will probably have higher fluoride concentrations compared to other igneous rocks. Most minerals that contain fluoride are not highly soluble and are often present in resistate sediments. Older waters often have higher concentrations of fluoride through water rock interaction over a long period of time. Adsorption can occur on kaolinite, however, this is insignificant below pH 4. Above pH 7.5 desorption can occur (Hem, 1992). Fluoride replaces the OH^- ion in kaolinite. The OH^- ion has a lower electromotive force (emf) than fluoride, therefore will only be liberated under thermal conditions (T. Horton, pers. comm., 2008).

Fluoride concentrations in O28w/0219 are very low considering the old age of the water, two samples were less than the minimum measureable concentration and the other sample consisted of only 0.45 mg/L. This equates to approximately one third of average seawater concentrations.

It is likely that fluoride has adsorbed to the kaolinite identified in O28w/0219 as the saline samples are within the pH 4-7.5 range, which allows for fluoride adsorption.

5.3.11 Arsenic

High natural arsenic concentrations are generally found in geothermal waters, closed basins or semi-arid areas, and strongly reducing aquifers. Groundwater flow in these areas is often sluggish allowing arsenic released from the sediment to accumulate. Arsenic will be released in significant concentrations into the groundwater if either the pH is greater than 8.5 leading to desorption of arsenic from mineral oxides or from the reductive dissolution of iron and manganese in strongly reducing waters (Hem, 1992). Within an aquifer, arsenic concentrations can vary considerably spatially and over time (Smedley & Kinniburgh, 2001).

Two of the sample from O28w/0219 showed concentrations lower than the minimum measurable concentration, while one sample showed concentrations twice the allowed New Zealand Drinking water standards (Ministry of Health, 2005). This is thought to reflect the variation of arsenic in the deep saline water. Two possible sources for the arsenic concentrations in the deep saline water, the strongly reducing conditions reflected by the high iron, manganese, boron, methane and the very low sulphate which could allow desorption of arsenic from the Torlesse gravels (mean = 5.6 ppm arsenic). Very high arsenic concentrations are related to calcite veins and fault gouge in the Main Divide from the upward movement of deep crustal fluids (Horton *et al.*, 2001). If geothermal water was the source of the high salinity migrating upward along the fault they probably would consist of high arsenic values as seen in one O28w/O219 sample. However, calcium concentrations are probably not from dissolution of calcite due to the low bicarbonate in the samples. Any fault related water would be expected to have higher levels of arsenic. Pedogenic carbonate formation during the last glacial maximum identified in Canterbury loess horizons (Almond *et al.*, 2007) suggest arid climatic conditions at the time of deposition. It is likely that if at that time the Canterbury Plains were in an arid environment during the last glacial maximum that the Wairau Valley was also a semi-arid to arid environment as it has greater protection from rainfall from the Richmond Ranges along the northern of the valley. It is possible that if the salinity formed under these conditions (concentration through evaporation) that arsenic also formed during this time in the.

5.3.12 Nitrogen

Samples from O28w/0219 were analysed for both ammoniacal nitrogen and nitrate nitrogen. Concentrations for both ions were consistent between the three samples analysed (Table 5.1) showing very low nitrate nitrogen and elevated ammoniacal nitrogen concentrations. Nitrogen in the form of ammoniacal nitrogen is reflective of the anoxic condition of the deep saline water (Close *et al.*, 2001).

5.3.13 Silica

Crystalline SiO_2 is a major component of most igneous rocks and sandstone, however, it is highly resistant to weathering by water. High temperature waters improve the solubility of silica to solution. Morey *et al*, (1962) suggest SiO_2 solubility is 6 mg/L at 25°C and 26 mg/L at 84°C. Seawater contains silica concentrations of less than 1 mg/L at the surface due to uptake from micro-organisms. Natural waters generally have silica values in the range of 1-30 mg/L (Hem, 1992).

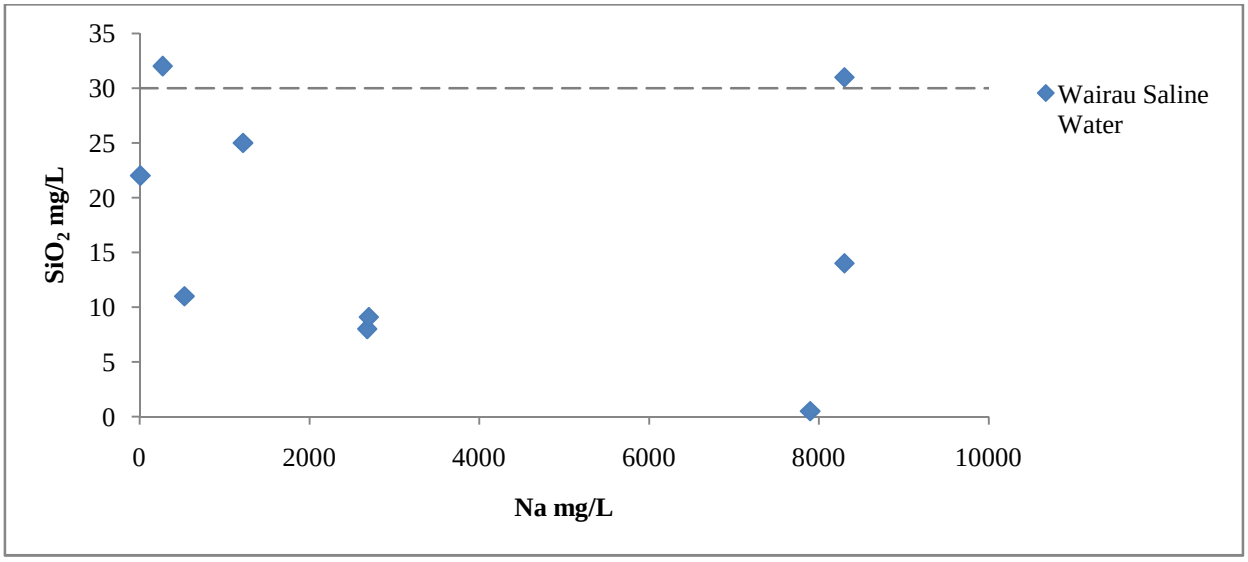


Figure 5.7: Silica verse Sodium in the Wairau Valley saline waters, dashed line represents Si equilibrium concentration for silicate rocks (Rosen, 2001).

Figure 5.7 is a silica verse sodium diagram of the saline waters in the Wairau Valley. It shows no relationship between silica and sodium which are often correlated in New Zealand waters from silicate weathering (Rosen, 2001). The three samples with the highest sodium concentrations are from O28w/0219, these show significant spread. However, due to the old age of the water it is

most likely that the value closest to silica equilibrium is the most reliable. Despite the variation in O28w/0219, no values are significantly elevated to suggest a geothermal influence, all are close to or below silica equilibrium for silicates. Thermal water derived from Torlesse Terrane in the South Island of New Zealand all show elevated silica concentrations, well above the levels present in the Wairau Valley saline water samples.

5.3.14 Boron

Thermal springs related to volcanic geology often have elevated boron due to associated volcanic gasses (Hem, 1992), high temperature processes are also required to increase the dissolution of boron (Morgenstern *et al*, 2007). Tourmaline is the only boron mineral readily found in soils, however it is highly resistant to weathering. Seawater contains 4.6 mg/L boron and is generally the most common source of boron in natural waters via intrusion or sea spray. During evaporation of seawater boron related minerals never reach saturation, furthermore, its hydrated form is highly soluble precluding significant concentrations to develop in slow moving groundwaters. Boron is preferentially absorbed or adsorbed by clay minerals at low temperatures (Hem, 1992). These can then be flushed by fresh water releasing the boron back into the groundwater, however, below pH 8.7 $B(OH)_3$ is not easily adsorbed by clay minerals (Hounslow, 1995).

Boron concentrations in O28w/0219 are very high (18 mg/L) compared to Southern Hills and Wairau River water (less than 0.1 mg/L). Samples from O28w/0219 are approximately four times higher than seawater. Figure 5.3 shows some correlation between boron and chloride concentration, however, this does not correlate with seawater enrichment. Morgenstern *et al*, (2007) suggest groundwater requires reducing conditions and contact with Torlesse basement for high boron concentrations as recognised in the Flaxbourne Catchment in southeast Marlborough. O28w/0219 reflects reducing conditions with very high iron and manganese concentrations, very low sulphate and high methane. The water is also significantly old enough for boron concentrations to accumulate, therefore, this is probably the source of the boron in O28w/0219. The pH is low enough that adsorption is not removing boron from the water.

5.4 Groundwater Classification

5.4.1 Graphical Presentation of Chemical Analyses

When presenting the major ion concentration of the Wairau Valley waters both stiff plots and piper diagrams are used to aid in the evaluation and classification of water type. Both methods are presented in this study as they are widely used by hydrogeologists to evaluate and compare the groundwater chemistry of sampled waters.

5.4.2 Methodology and Application of Stiff Plots

A Stiff plot consists of four cation/anion pairs (Na+K – Cl; Ca – HCO_3; Mg – SO_4, and Fe – NO_3) plotted on parallel horizontal axes. Concentrations are plotted in milliequivalents per litre (meq/L) to allow comparison between the different ions. Each ion concentration extends out from a central vertical axis equal to 0, plotted values are connected to give an irregular shaped polygon characteristic of a specific groundwater type reflected both in shape and size of the polygon (Fetter, 2001).

A distinct groundwater classification can only be assigned to a stiff plot sample where there are clearly dominant cations and anions. This does not always occur and concentrations may be very similar. Where the relative cation and anion concentrations do not vary by more than 50% the sample would have no dominant cation or anion (Hem, 1992). If no dominant cation or anion is present it is often the result of mixing between at least two different water types. Stiff plots are excellent for quick differentiation between samples and identifying waters which originate from a single source

5.4.3 Methodology and Applications of Piper Diagrams

The trilinear piper diagram consists of three plotting areas, two triangular areas with one each for cations and anions. The diamond shape area displays data projected from the two triangle plots, each side representing a cation or anion pair (sodium + potassium, calcium + magnesium). Data is derived from ionic concentrations (meq/L) plotted on a scale ranging from 0 to 100 representing a percentage of the total anions or cations (Fetter, 2001). The projected data point in the diamond represents the water type of that sample. Where mixing has occurred between two end member water types, samples will plot on a straight line in the direction of the cation/anion

vertices indicating the cation or anion enrichment for the more concentrated samples (for example bicarbonate).

The Piper method is excellent for comparing large sample sets for evaluating hydrochemical facies of selected waters, furthermore. Piper diagrams are a useful tool when assessing whether sample could be the result of mixing or is affected by solution-precipitation reactions (Loris, 2000). However, it does not indicate the total dissolved solids for each sample.

5.4.4 Stiff Plots

Figure 5.8 shows Stiff plots for selected chemical samples. Stiff plots are constructed with the computer software program Grapher 7. From examination of Stiff plots, groundwaters and surface waters can be classified into 4 groups: sodium bicarbonate type, calcium bicarbonate type, sodium chloride type, and non dominant type waters.

5.4.4.1 Stream Chemistry

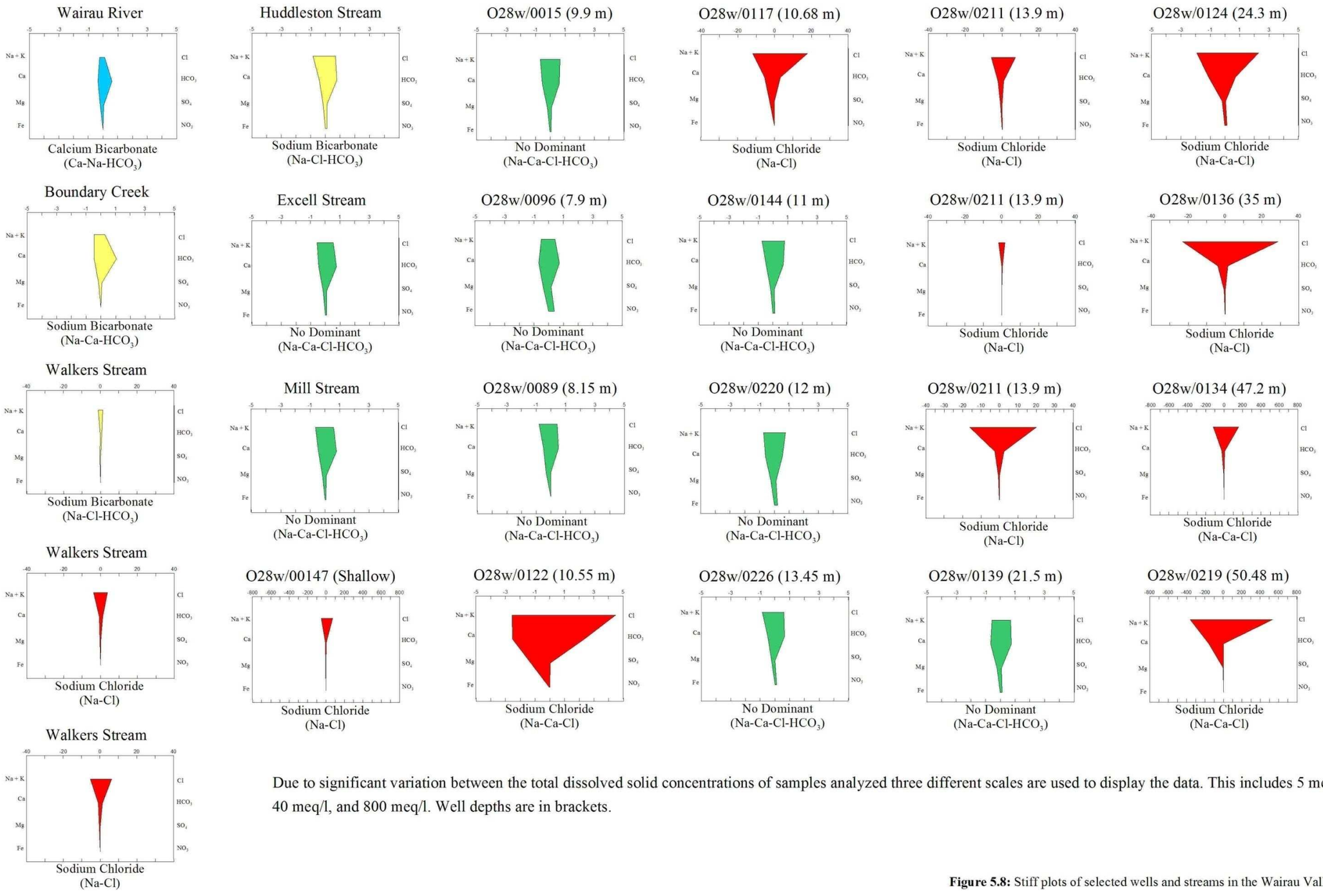
Wairau River water is the only calcium bicarbonate sample, however, it does show a similar shape polygon to Boundary Creek. The total dissolved solids are less in the Wairau River sample compared to all South Hill streams analysed. The Boundary Creek sample is the only Southern Hills stream sample that is was collected away from the Wairau Valley floor, therefore, has not become contaminated from localised salinity within the valley. The Boundary Creek sample is probably a good representation of the dissolved solids composition of all local Southern Hill Streams prior to reaching the Wairau Valley groundwater system. Huddleston Stream, Mill Stream, and Excell Stream all show a slight increase in sodium and chloride when compared to Boundary Creek. As discussed in Chapter Two Boundary Creek, Excell Stream, and Huddleston Stream are ephemeral on the valley floor and all stream flow enters the groundwater system upon entering the Wairau Valley. It is likely that interaction with valley sediments yields the sodium and chloride ions considering the significant quantities present at the surface and at depth south of the Wairau Fault. It is important to note that the quantities considered here are still very low and water in these streams and related springs is of very high quality.

5.4.2.2 Well Chemistry

Wells analysed include O28w/0015, O28w/0096, O28w/0089, O28w/0122, O28w/0117, O28w/0144, O28w/0220, O28w/0226, O28w/0211, O28w/0139, O28w/0124, O28w/0136, O28w/0134, and O28w/0219 (Figure 5.1). All wells are either non-dominant facies or sodium chloride facies type waters. Generally these can be separated with depth, however, it is difficult to define the level to which the change occurs in the Wairau Valley because of the separation between the wells. Wells O28w/0117, O28w/0122, and O28w/0147 are all no more than 11 m deep and are dominated by sodium and chloride ions, and also calcium in O28w/0122. The geographic distribution of these 3 wells suggests the most likely reason for this is because of their close proximity to the fault trace which is possibly a conduit for deep water to migrate upward. Furthermore, groundwater between the Wairau Fault and the Southern Hills is pushed upward relative to the rest of the valley. This is due to the fault dipping approximately 85^{o} S and trending into the bedrock of the Southern Hills effectively acting as a wedge as groundwater flows down valley.

Wells O28w/0015, O28w/0096, O28w/0089, O28w/0122, O28w/0117, O28w/0144, and O28w/0220 are all less than 12 m in depth north of the Wairau Fault and generally show chemistry similar to that of Mill Stream and Excell Stream.

O28w/0124 and O28w/0211 screen to depths of 24.3 m and 13.9 m respectively, both wells are sodium-chloride type. O28w/00124 has low total dissolved solids, while O28w/0211 shows some variation of the three samples analysed from 125 mg/L to over 1315 mg/L. This fluctuation is probable for wells which screen within the mixing zone through seasonal variation in groundwater flow. O28w/0124 contains 213 mg/L for the one sample analysed and show increases in sodium, chloride, calcium, and boron which all reflect a saline influence. Comparing O28w/0124 with conductivity readings collected during drilling of O28w/0219 show the variation in depth to saline water over a short distance. Small variations in the total dissolved solids are probable in this well, however, as it is probably very close to the boundary between saline and fresh water. Well O28w/0139, at 21.5 m, is the deepest well of non dominant type water and is probably close to the saline fresh water boundary, however, further investigation is required to better define the depth to saline water at this location.



Due to significant variation between the total dissolved solid concentrations of samples analyzed three different scales are used to display the data. This includes 5 meq/l, 40 meq/l, and 800 meq/l. Well depths are in brackets.

Figure 5.8: Stiff plots of selected wells and streams in the Wairau Valley.

5.4.5 Piper & Hydrochemical Facies Classification

Selected groundwater and surface water sample analyses are plotted in a Piper trilinear diagram in Figure 5.9 Well locations and stream sampling sites are presented in Figure 5.1. Boundary Creek and Wairau River samples contain the lowest proportions of chloride and the only samples analysed for which bicarbonate is the dominant anion. Wairau River samples plot as calcium-bicarbonate type water with one on the intersection between three different facies types. Boundary Creek water plots within calcium-sodium-bicarbonate facies and as stated earlier is the only sample that is derived from the Southern Hills prior to reaching the Wairau Valley groundwater system, it is considered representative of Southern Hills water composition. The predominant rock type in the Wairau River catchment is Torlesse sandstone and the similar chemistry is thought to be representative of this rock type.

5.4.5.1 Non-Dominant Waters

Excell, Huddleston, and Mill streams along with wells O28w/0015, O28w/0089, O28w/0139, O28w/0144, O28w/0220 and O28w/0226 are all calcium-sodium-bicarbonate-chloride type (no dominant type) water. All of these waters are recharged from Southern Hills runoff which is similar in composition to Boundary Creek water. This water is of very high quality, but the trilinear plot suggests it has moved to being more sodium-chloride dominant. It probably inherits the sodium and chloride influence during groundwater flow south of the Wairau Fault, resistivity tomography surveys completed for this study (Chapter Three) indicate the depth to saline water between the Wairau Fault and the Southern Hills in the study area is shallower compared to the rest of the valley.

5.4.5.2 Sodium Chloride Waters

Samples from Walkers stream are sodium-chloride waters however they show some variation within this facies type, one sample is separated from the other two Walkers Stream samples with the lone sample plotting closer to the centre of the diamond. Two reasons can explain this variation; conductivity in Walkers Stream is known to spike during rainfall events at the Parsons Road Bridge and the samples are representing this variation. Secondly, the variation could be a result of geographic distribution of the sample sites. The sample upstream of the Parsons Road bridge crossing Walkers stream contains the lowest chloride concentration, the high salinity in Walkers Stream probably results from surface runoff during rainfall events from where Walkers

Stream breaks the fault trace, and this is where saline water is present at the surface for most of the year. Appendix 5.2 shows conductivity data for Walkers Stream over July/August 2006 at the Parsons Road Bridge.

Wells O28w/0117, O28w/0122, and O28w/0124 are calcium-sodium-bicarbonate type water. O28w/0134, O28w/0136, O28w/0147, O28w/0211, and O28w/0219 are sodium-bicarbonate water type. These wells all reflect a significant influence from the saline water in the valley. O28w/0219 shows the highest total dissolved solids and is significantly higher than other samples from the Wairau Valley.

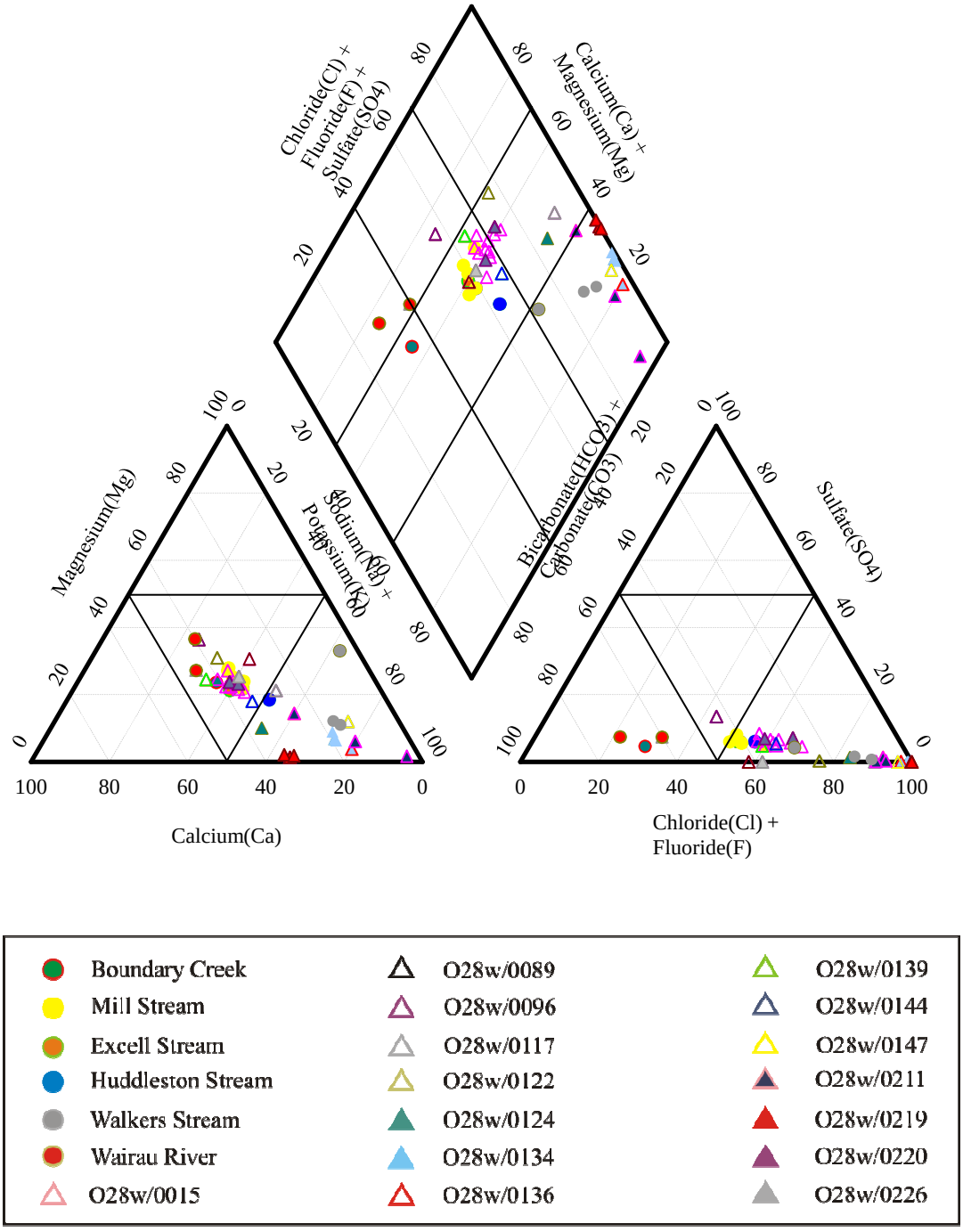


Figure 5.9: Piper plot of waters in the Wairau Valley.

5.5 Chapter Summary

Saline groundwater in the study area contains elevated concentrations of sodium, calcium, iron, chloride, bromide, manganese, arsenic, and boron. Potassium and magnesium are low relative to seawater but slightly elevated relative to Wairau River and southern Hills waters. Saline samples are very low in sulphate and fluoride. Concentrations of sodium, calcium, and bromide are thought to be related to chloride due to the strong correlation each ion has relative to the chloride concentration. Elevated iron, manganese, and boron with very low sulphate are thought to reflect strongly reducing conditions.

Southern Hills streams show sodium bicarbonate to no dominant type with the exception of Walkers stream which is sodium chloride type. The piper plot indicates Boundary Creek as being the most similar to Wairau River water, this is thought to be a result of the sampling location which was off the valley floor and the water had not interacted with the south bank groundwater system in any way.

Well samples shallower than 12 m are no dominant facies type, wells greater than 20 m are generally sodium chloride facies type, however, there are some exceptions. Shallow wells in close proximity to the Wairau Fault trace generally have a sodium chloride facies type. Firm conclusions on variations with depth are difficult due to the low number of wells. The change between no dominant type fresh waters and sodium chloride saline waters will probably vary throughout the valley.

CHAPTER SIX

SYNTHESIS

6.1 Introduction

Chapter Six aims to bring together the data introduced from Chapters Two through Five and relate them to the major objectives of this investigation. These include; defining the recharge flow path of the Southern Hills runoff to the Wairau Valley Aquifer; the extent of the saline water at the Mill Road/Parsons Road cross section; and defining the origins of the high salinity in the Wairau Valley. Potential sources of the chemical constituents include formation water of marine origin, evaporative concentration of fresh water, water rock interaction, and metamorphic or hydrothermal waters.

6.2 South Bank Groundwater Flow Model

Southern Hills runoff has been identified as the recharge source for the Wairau Valley Aquifer below the Holocene Wr 1 terrace surface (Taylor, 2003). One aim of this investigation is to identify the groundwater flow paths recharged by Southern Hills runoff. Figure 6.1 is a schematic diagram of the groundwater flow from the Southern Hills runoff to the Wairau Valley Aquifer. This interpretation is based on aerial photo interpretation, geomorphology, geophysical surveys and stream gauging of the south bank tributaries.

6.2.1 Wairau Valley Aquifer Recharge

The high permeability gravels that represent the Wairau Valley Aquifer are located south of the major terrace riser between Wr 1 and Wr 2 terrace surfaces. The Wairau Valley Aquifer gravels consist of between 15-20 m of reworked Speargrass Formation gravels which contain lower proportion of fines relative to non-reworked Speargrass formation and a significantly higher hydraulic conductivity as outlined in Chapter Two.

The occurrence of springs along the fault trace, as described in Chapter Two, and the Multi-Electrode resistivity (MER) surveys (Chapter Three) across the Wairau Fault trace which show a drop in the depth to saline water crossing the fault from south to north, this suggest that the Wairau Fault is acting as a semi-permeable barrier to groundwater flow. Zachariasen *et al.,* (2006) found no trace of a fine grained gouge during trenching across the fault. There is no change in the valley gravels either side of the fault, the low permeability is probably controlled by imbrication of the gravels due to right lateral movement on the fault. Groundwater flow in the Speargrass gravels, below the Wr 2 terrace surface, is largely controlled by northeast trending buried channel deposits. The approximate trend of the buried channels intersects with the Wairau Fault. These buried channels may be acting as conduits for groundwater movement across the fault. The intersection point between the fault and the channel deposits is unknown, although they are possibly related to Excell and Huddleston streams and potentially Walkers stream where its surface flow is diverted by the Wairau Fault. The upper terrace groundwater system is considered separate from the lower terrace groundwater system at the Mill Road/Parsons Road cross section, however, they are related by the same recharge source, Southern Hills runoff.

Boundary Creek is the largest Southern Hills tributary in the study area. The surface flow characteristics are discussed in detail in Chapter Two. Aerial photo interpretation shows the extent of reworked Speargrass gravels by Boundary Creek streamflow. As Boundary Creek enters the valley the channel trends approximately north until the fault trace where it turns to a northeast trend. Boundary Creek has eroded the Wairau Fault trace and the major terrace riser separating the Wr 1 and Wr 2 terrace surfaces suggesting a possible zone of reworked gravels related to Boundary Creek. This reworked zone could potentially transfer water to recharge the Wairau Valley Aquifer. Due to the trend of Boundary Creek it will capture all shallow down valley groundwater flow that exists south of the Wairau Fault. However, this is not considered very significant in relation to the total water balance. Groundwater traversing the fault northeast of Boundary Creek would be incorporated into the upper terrace groundwater system. Reworked Boundary Creek gravels are probably relatively thin, although, without further investigations the actual thickness is unknown.

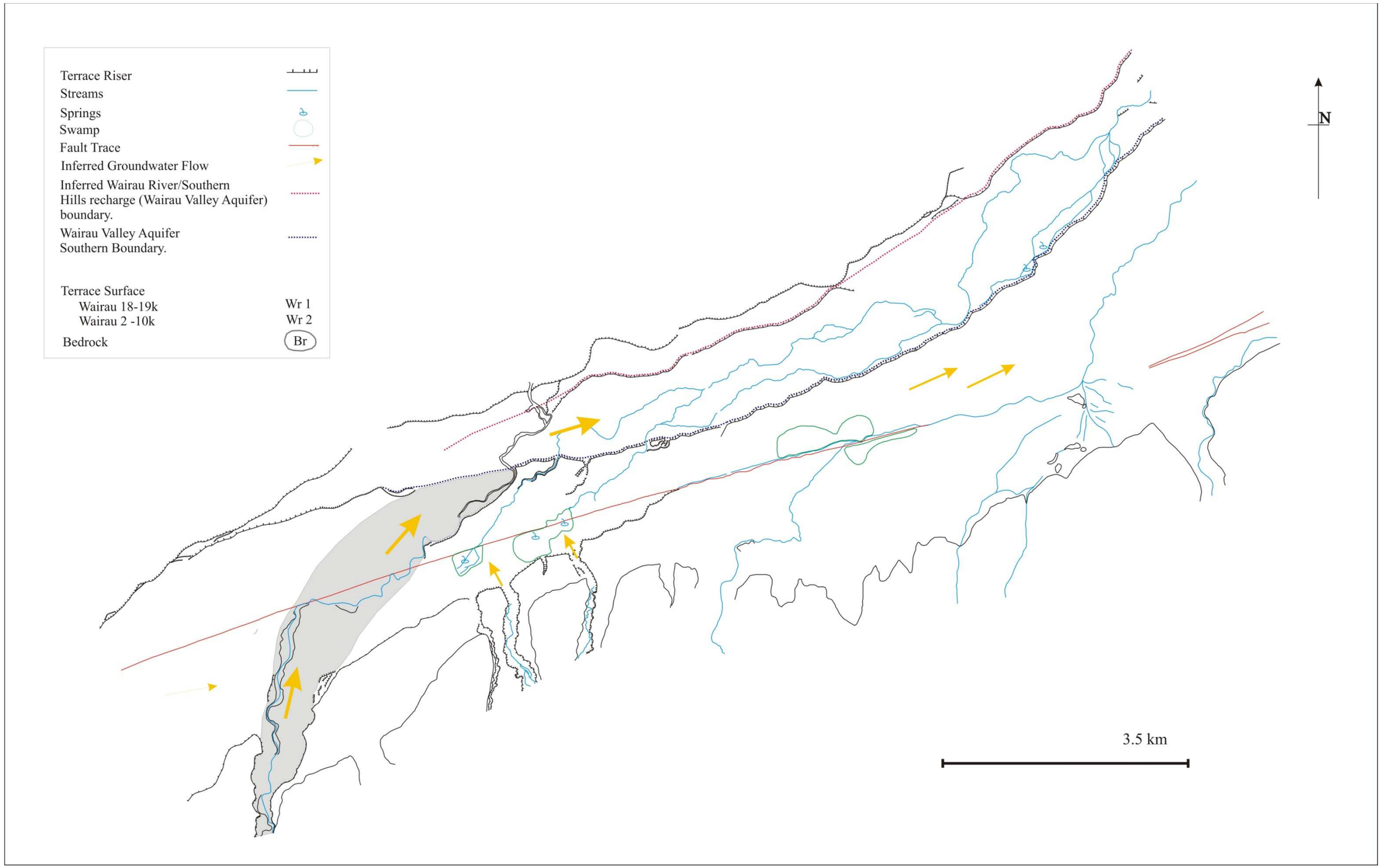


Figure 6.1: Schematic map of the shallow groundwater flow for the Wairau Valley south bank.

6.2.2 Extent of the Saline Groundwater

Defining the spatial extent of the saline water at the Mill Road/Parsons Road is key to understanding the nature of the saline groundwater and its relationship to the Wairau Fault. Highly saline waters dominated at depths greater than approximately 15-20 m below the Wr 1 terrace surface. The change from shallow fresh water is gradational with a thin brackish mix zone present below the Wairau Valley Aquifer. Below the Wr 2 terrace surface the freshwater/saline water profile becomes more complicated. Salinity of the groundwater along the south bank is thought to be controlled by the hydraulic conductivity of the gravels and the availability of a fresh water source to flush the gravels. Between the Southern Hills and the Wairau Fault, in the study area, the depth to saline water is much shallower than the northern side of the fault. This is thought to be the result of the Wairau Fault trending into the Southern Hills forming a wedge, as the groundwater flows down valley this wedge forces deeper water upward relative to the rest of the valley.

Survey lines 2 and 3, across the Wairau Fault trace, show an apparent plume of saline groundwater between the fault trace and the Southern Hills. This is represented by a series of contour increasing in resistivity from the base of the profile (as shown in Chapter Three). Survey line 3 consists of a roll-on survey across the fault giving a complete image of the resistivity of the subsurface around the inferred fault trace at depth. This shows a clear relationship of the fault with very low resistivity values and could indicate that saline water is derived from the Wairau Fault at depth. Saline water migrating up the Wairau Fault within the secondary porosity in the basement rock may be partitioned upon entering the valley gravels as the fault expression in the valley inhibits natural groundwater movement due to imbrications of gravels. The wedge effect described earlier may be acting to bring the saline groundwater to a higher elevation relative to the northern side of the fault. The base of the MER surveys do not reach basement and similar low resistivity contours may be present north of the Wairau Fault below the maximum depth imaged by the MER profiles as there is more room space for upward migrating saline fluid to spread. The plume on the southern side of the fault may also represent the setting shown if where secondary porosity is largely in the footwall southern fault block, as a result saline water enters the valley south of the valley expression of the Wairau Fault. Further investigation close to the fault is required to define this further. It is possible the apparent plume is not a representation of

the actual conditions and is an artefact of the inversion process. However, the similarities between surveys 2 and 3 suggest that it is probably representative of the groundwater system.

6.3 Origins of the Wairau Valley Salinity

The hydrochemistry of the saline samples in the Wairau Valley are analysed in Chapter Five. Analysis of the most conservative components and selected major ions gives an insight to the source of the chemical constituents. Stable isotope analysis, including ^{13}C, ^{18}O, and D can indicate the origins of the fluid. This is an important distinction as the origins of the fluid and chemical constituents may not necessarily be related. The hydrochemistry of the saline water is complex and could potentially be derived from several different sources including Formation water, evaporative concentration of fresh water and dissolution of salt within the Wairau Valley, metamorphic/hydrothermal waters, or through water/rock interaction over long residence times. This section discusses the potential for each of these water types as a source of the salinity.

6.3.1 Formation water

6.3.1.1 Nature of formation waters

Formation water, or basinal brines, are defined as old saline water found in large sedimentary basins where basin sediments are typically marine in origin. Formation waters are generally found at depths between 500-3700 m. The salinity of formation water can vary from close to seawater up to a highly saline Ca-Na-Cl brine with total dissolved solids greater than 100,000 mg/L (Hoefs, 2004). The origins of formation waters are highly debated and several possible sources have been put in forward in the literature (Clayton *et al*., 1966; Rittenhouse, 1967; Hanor, 1983; Appelo & Postma, 1993; Richter & Kreitler, 1993; Whittemore, 1995; Whittemore, 2007). Defining the initial source in formation water is difficult due to the complex history and processes that have altered the chemistry post emplacement. Hydrochemical and isotope analysis are frequently used in hydrological studies to differentiate between formation waters and other potential saline contaminant sources.

Formation water generally show an $\delta^{18}O$ and δD relationship along a positive regression from local meteoric water. This is often correlated with salinity, the samples with the lowest salinity are closest to the local meteoric water line. Formation waters may consist of complete replacement of original water with local meteoric water so the $\delta^{18}O$ and δD regression is not a

reflection of the source of the fluid but a result of subsequent processes (Clayton *et al.,* 1966). The regression may also represent a mixing line between meteoric water, and either fossil seawater or seawater enriched in ^{18}O and D from evaporation (Knauth & Beeunas, 1986; Knauth, 1988). Water rock interaction could explain the ^{18}O-shift over time. This is supported by the correlation between ^{18}O enrichment and total dissolved solids (Appelo & Postma, 1993; Hoefs, 2004). However, hydrogen fractionation is more difficult to explain and not well understood in formation waters.

Geochemical ratios are excellent tools to differentiate between potential saline sources. Whittemore (1995) suggests mass ratios of Br/Cl, and SO_4/Cl are good indicators of the saline source. Richter & Kreitler (1993) suggest several mass ratios and bivariate plots of characteristic mass ratios to delineate between different salinity sources, including Br/Cl, Mg/K, Na/Cl, SO_4/(Na+K), Na/Ca, Mg/Cl, Ca/Mg, K/Cl, Ca/Cl, and Na/K. The Na/Cl mass ratio has been used extensively as an indicator to distinguish between seawater, halite solution and formation water. The Na/Cl mass ratio for pure halite is 0.648. Modern seawater has a mass ratio of 0.56, and formation waters generally plot close to 0.48 or lower (Figure 6.2). Samples contaminated with seawater or halite solution brine will show a very strong relationship due to their relatively uniform chemistry. Greater variation in Na/Cl for formation waters is common, however, they are generally lower than seawater or halite solution due to reverse cation exchange processes removing sodium from solution (Richter & Kreitler, 1993).

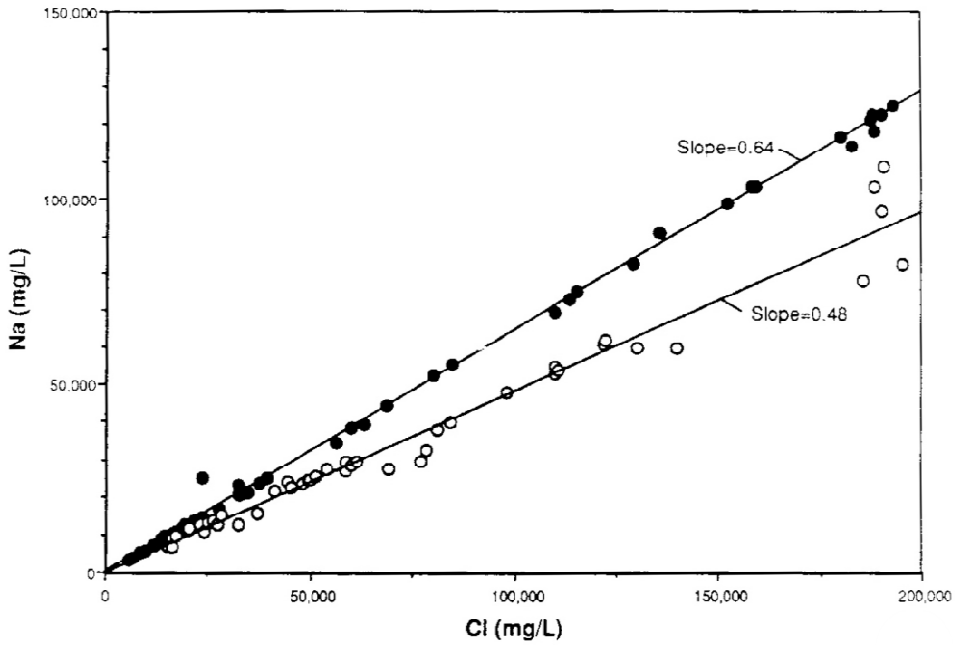


Figure 6.2: Sodium versus chloride plot for halite solution waters (black dots) and formation waters (hollow dots) in saline groundwater samples from USA (Richter & Kreitler, 1993)

Due to the highly conservative nature of bromide and chloride, the ratio of the two ions is a very good indicator of the initial solute source. Table 6.1 shows Br/Cl ratios from various natural waters. If seawater was the source of contamination the Br/Cl ratio would be very close to 0.00347 and maybe slightly higher as bromine is released from marine organisms. The Br/Cl mass ratio of water derived from halite dissolution does vary depending on its concentration in solution. During early halite precipitation the Br/Cl mass ratio is between 0.00008-0.00009. However, later stage precipitation has a Br/Cl mass ratio between 0.0008-0.001. Formation waters show the most variation in their Br/Cl mass ratios due to the different sources for the salinity. Formation waters derived from connate seawater are often higher than the seawater ratio due to the release of bromide from organic matter during diagenesis (Whittemore, 1995). Dissolution of evaporite beds at depth will result in Br/Cl mass ratios approximately two orders of magnitude lower than the seawater ratio (Hem, 1992).

Table 6.1: General range in chloride concentration and Br/Cl mass ratio for selected saline water sources.

Source	Cl (mg/L)	Br/Cl mass
Fresh Surface water and groundwater	0.1-100	0.0003-0.1
Seawater	19,350	0.00347
Natural evaporaite dissolution	10,000-250,000	0.00006-0.0005
Formation water	<10,000-270,000	0.0005-0.04

6.3.1.2 Formation water as the source of the Wairau Valley Saline Groundwater

Isotope data from the saline well in the study area shows several similarities to formation waters found in other parts of the world, however, there are also some key differences which help define the source of the salinity.

Figure 6.3 shows characteristic bivariate ratio plots for saline Wairau Valley waters compared to formation waters and evaporite waters found in several states throughout the USA. The Wairau Valley waters show a very similar chemistry compared to the formation waters across all plots. These plots take into account the cations; sodium, potassium, magnesium, calcium, and the anions; chloride, sulphate, and bromide, which are all important constituents in formation waters. The distinct regions in these plots between formation and evaporite waters and the consistency for all ratio plots suggest fault derived formation water is a potential source of the salinity in the Wairau Valley.

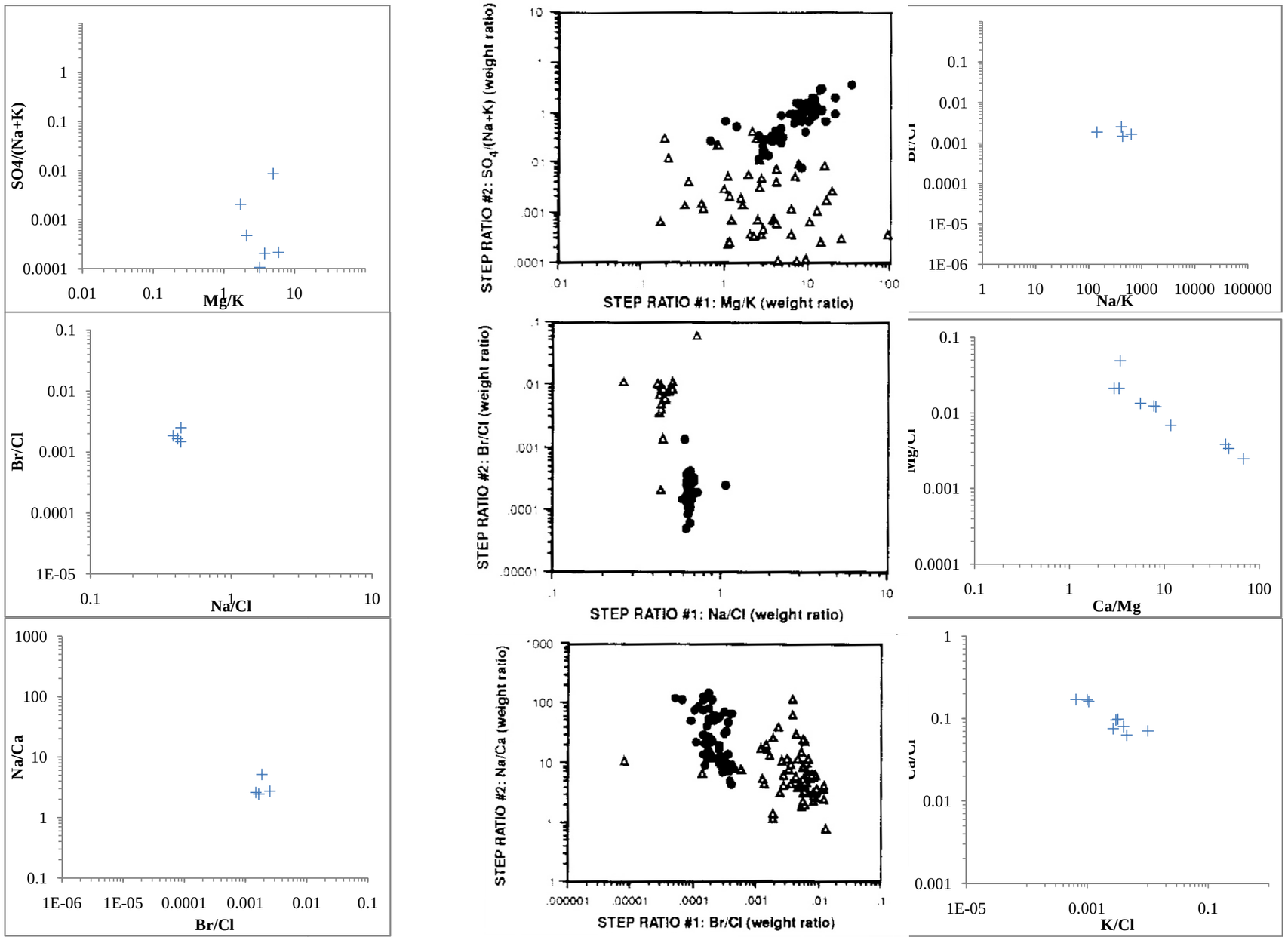


Figure 6.3: Bivariate plots of ratios which best define halite solution brines from formation brines. Plot of saline wells in the Wairau Valley (blue crosses) is acompanied by a plot of selected brines identified in the USA for comparison, in these plots open triangles represent formation water and filled circles indicate halite solution brines (non-Wairau plots from Richter & Kreitler (1993))

Br/Cl ratios for the Wairau Valley saline waters (Figure 6.4) are slightly lower than seawater but within the same order of magnitude. Davis *et al.*, (1998) suggests that it is very difficult to reduce the Br/Cl ratio due to the chemical characteristics of bromide and chloride, as described in Chapter Three.

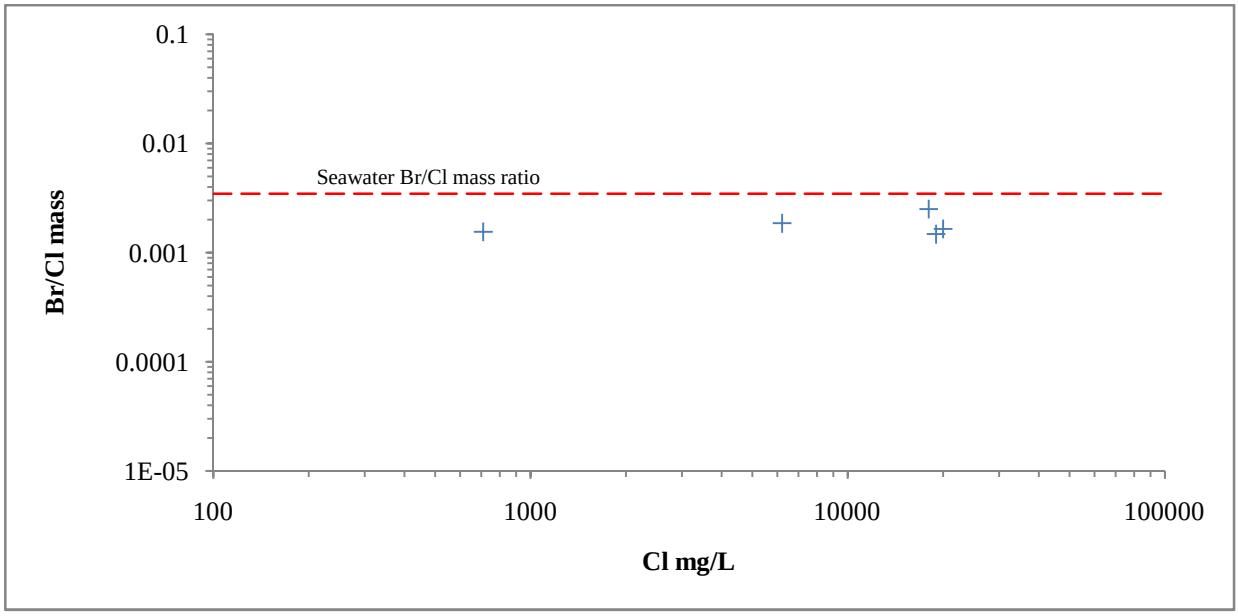


Figure 6.4: Br/Cl mass ratio versus chloride for saline wells in the Wairau Valley.

Inferring seawater as a source of the salinity, two origins are proposed. These are a connate seawater derived from the Torlesse and infiltration of seawater into the fault when the coastline was within the valley.

Connate seawater had been proposed by Taylor (2003) as the source of the elevated salinity in the Wairau Valley. New data from this study, in particular isotope and hydrochemical analysis of well O28w/0219 further defines the source of the salinity.

Connate water is defined as water trapped in sediments at the time of deposition, commonly seawater (Hoefs, 2004; Richter & Kreitler, 1993). Taylor (2003) postulated that the isotope signature for a given chloride concentration could be determined from the strong correlation between $\delta^{18}O$ and chloride for three saline samples, and their relative isotope shift from average Wairau River composition (Figure 6.5). The samples which did not plot on this regression (Figure 6.5) were considered to have additional chloride from a source that did not

affect δ-values, for example, dissolved salt from evaporite rocks. From this relationship a sample with a chloride concentration approximately equal to seawater (19,000 mg/l) would have $\delta^{18}O$ and δD values of +6‰ and 0.0‰ respectively (Figure 6.6). In this scenario the seawater has undergone ^{18}O enrichment by +6‰ due to the water being in contact with rock over long residence times.

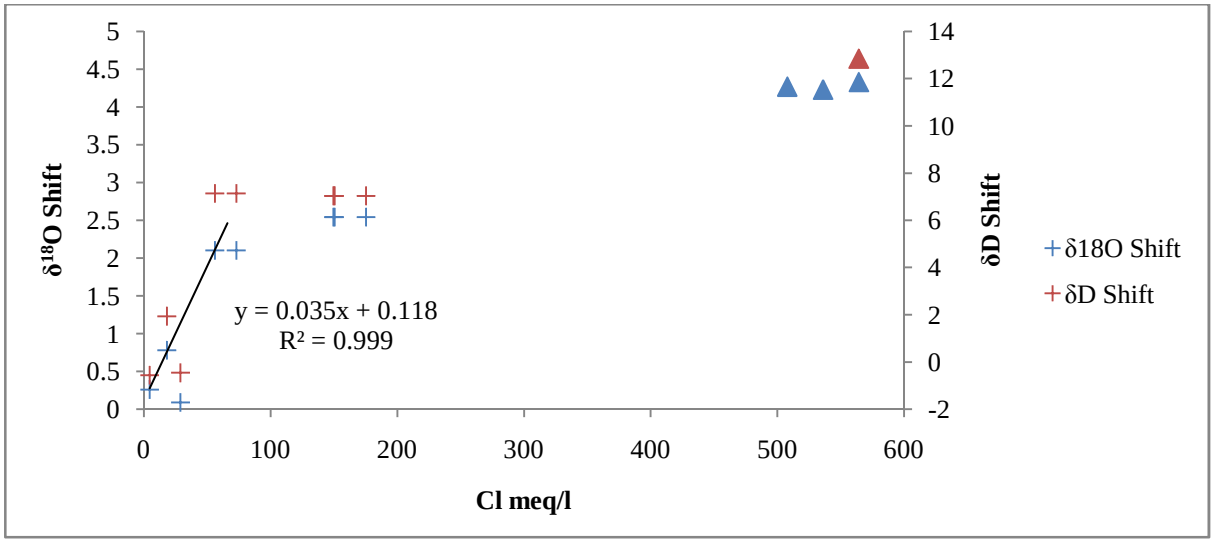


Figure 6.5: $\delta^{18}O$ and δD shift versus Cl for Wairau Valley saline water relative to Wairau River water. Modified from (Taylor, 2003). Triangles represent $\delta^{18}O$ and δD shifts versus Cl from O28w/0219.

Samples analysed from O28w/0219 show chloride values close to present day seawater concentrations, however, their $\delta^{18}O$ and δD values are significantly more negative than expected.

The regression between $\delta^{18}O$ and δD for saline wells is common for saline formation waters and shows that positive enrichment of $\delta^{18}O$ and δD is related to increasing chloride concentration. Clayton *et al*. (1966) suggest from the $\delta^{18}O$ versus δD regression that formation waters probably totally replace the initial source water by deep circulating meteoric water. The $\delta^{13}C$ value of -26 for well O28w/0219, introduced in Chapter Four, suggests that the water is terrestrial in origin. Furthermore, well O28w/0219 contains the highest salinities found in the Wairau Valley (29,014-31,952 mg/L) which is close to seawater concentrations. Formation water derived from connate seawater migrating into the Wairau Valley and mixing with meteoric water would result in $\delta^{13}C$ values for the most saline waters significantly closer to zero. Therefore, it is not likely that the saline water is the result of mixing between connate or fossil seawater and meteoric water. However, more $\delta^{13}C$ samples would better define the nature of the saline water.

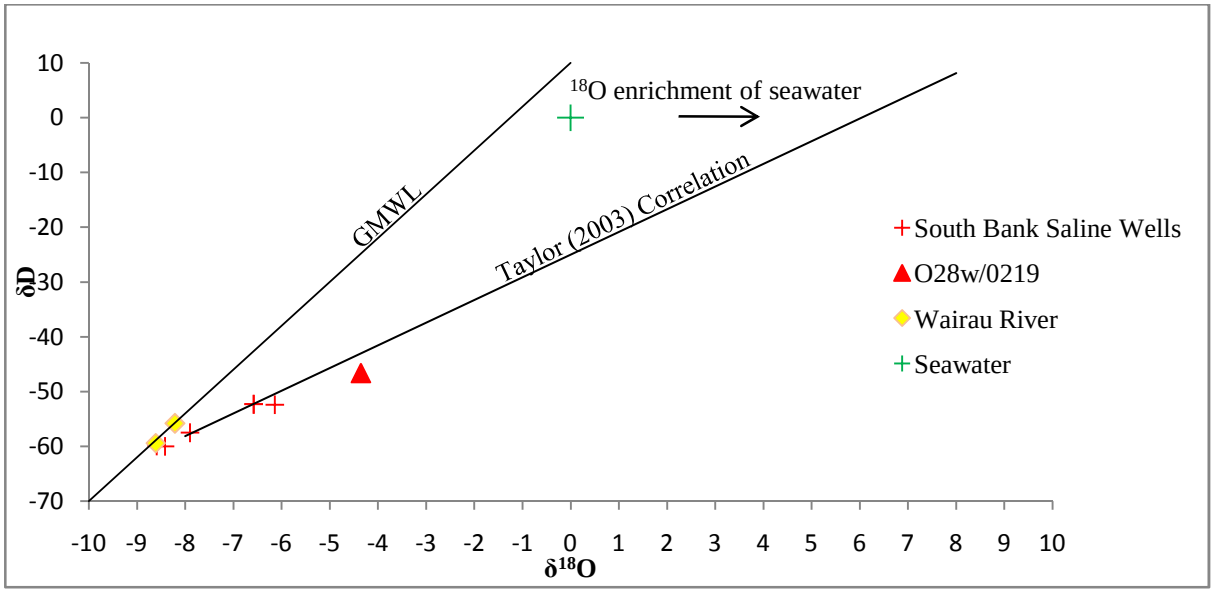


Figure 6.6: Wairau Valley saline water regression line extended to δD = 0, represents the possible isotope signature for old $\delta^{18}O$ enriched seawater mixing with Wairau River water. Saline regression line includes all saline well samples.

It is highly unlikely that Torlesse sandstone and argillite are capable of having significant quantities of connate water. The primary porosity of Torlesse is extremely low. The Torlesse Terrane is late Jurassic to early Cretaceous in age and has undergone regional metamorphism and diagenesis. Connate fluid from the Torlesse Terrane would have been subjected to these processes and, over an extremely long time period, exchange and removal of ions from the rock would lead to a water chemistry in equilibrium with Torlesse Terrane. This is discussed further in section 6.3.4.

Fossil seawater is old seawater which is not related to the sediments it is in. The isotopic signature and chloride composition suggest the Wairau Valley cannot be ^{18}O enriched connate seawater. However, there is potential that the relationship between chloride and $\delta^{18}O$ could reflect mixing between meteoric water and seawater which has developed through evaporative concentration at the surface before entering the fault groundwater system. Na-Cl-Br diagrams can identify whether a particular water has solutes derived from evaporative concentration of seawater or halite dissolution. Na/Br and Cl/Br ratios lower than seawater suggest evaporative concentration of seawater, whereas, higher ratios indicate halite dissolution (Walter *et al*., 1990; Chi & Savard, 1997). This is due to bromide enrichment in the residual brine and the very low

concentrations of bromide in halite deposits. Samples from the Wairau Valley wells have low bromide relative to sodium and chloride resulting in high Na/Br and Cl/Br ratios compared to seawater. This suggests that mixing between meteoric water and evaporative concentrated seawater cannot cause the $\delta^{18}O$ and δD regression in Wairau Valley samples. Wairau Valley samples plot above and to the left of the halite dissolution line. Sanchez-Martos *et al*., (2002) suggest the simplest solution for samples to move away from the dissolution/precipitation line is to reduce/enrich the sodium concentrations (Figure 6.7). Appelo & Postma (1993) suggest slight reductions of sodium concentration in formation waters can result from sodium fixation during clay diagenesis. Another explanation for the pattern in Wairau Valley samples is reverse cation exchange between sodium in the fluid and bound calcium. The three most saline samples from O28w/O219 plot along a very tight regression parallel to the dissolution/precipitation line. Other samples had significantly lower concentrations of constituents and may have been altered by dilution and mixing with another water source.

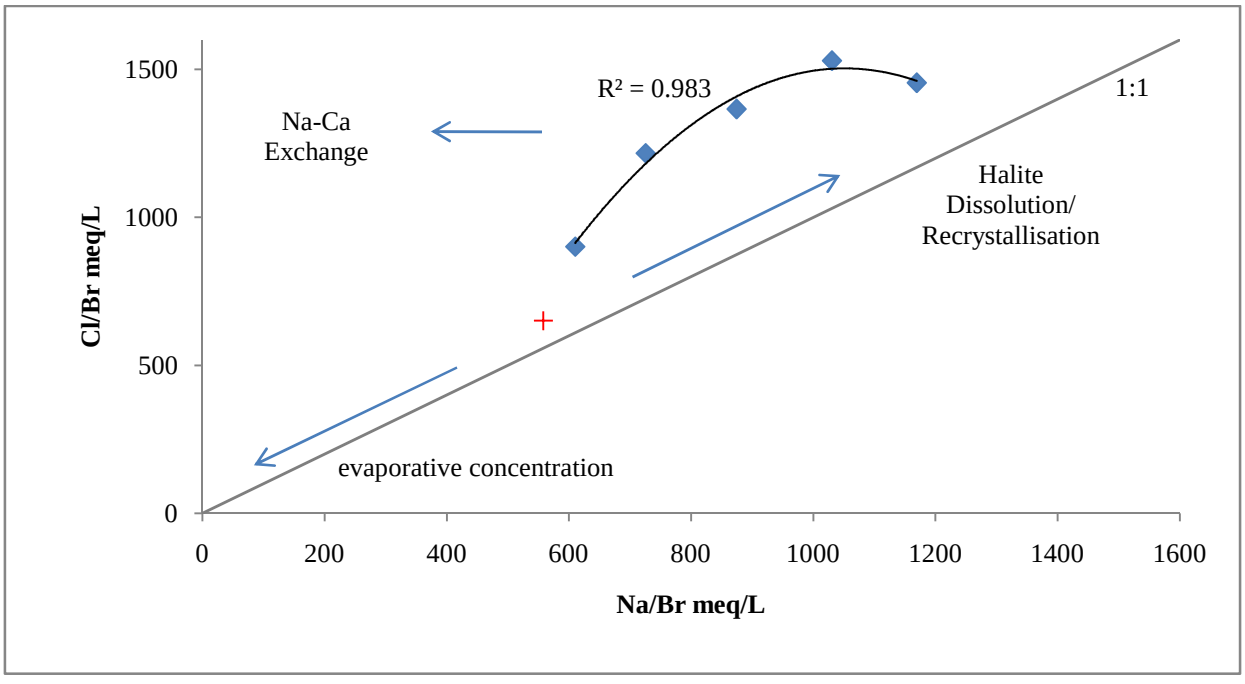


Figure 6.7: Na-Cl-Br diagram of selected saline wells in the study area.

6.3.2 Evaporative concentration within the Wairau Valley

Groundwater salinity in the Wairau Valley is potentially derived from evaporative concentration of fresh waters and salt dissolution within the valley during the Last Glacial Maximum. The physiographic setting of the Wairau Valley presented in Chapter Three suggests arid surface

conditions with low rainfall and potentially high evaporation rates, which could have enhanced the salinity of local surface waters in the Wairau Valley. Two processes are considered which could produce elevated salinity in an arid environment from a fresh water source. These are evaporative concentration of surface water held up in the valley and dissolution of salts during infiltration of meteoric water.

The $\delta^{18}O$ versus δD regression (slope = 3.4, R^2 = 0.97) for all Wairau Valley saline samples analysed in Chapter Four is a characteristic evaporation regression from local Wairau River water. Saline waters with chloride concentrations greater than 2000 mg/L clearly show a strong correlation between chloride and $\delta^{18}O$ (Figure 6.8), lower chloride concentrations are thought to be complicated by dilution.

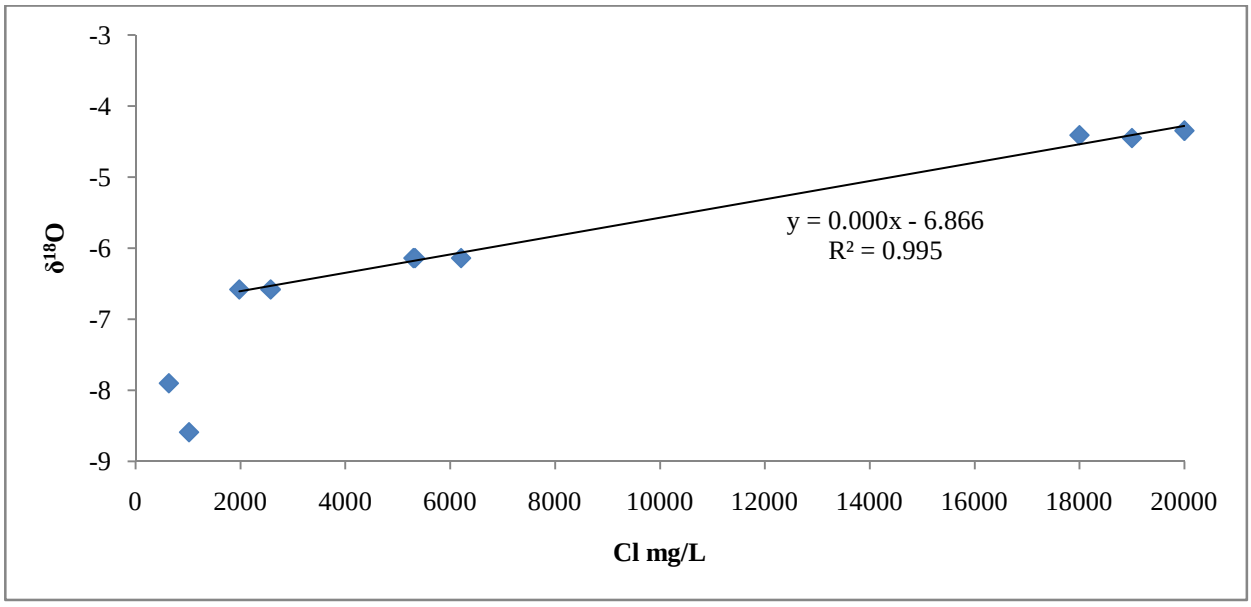


Figure 6.8: $\delta^{18}O$ versus chloride for saline wells in the Wairau Valley. The regression line is only for samples with a chloride value close to or greater than 2000 mg/L.

The Br/Cl ratios of the saline wells show no variation over increasing chloride concentrations (figure 6.4). This pattern is characteristic of concentration through evaporation which has not reached the stage of halite precipitation (Davis *et al.*, 1998). Br/Cl mass ratio of fresh waters (less than 10 mg/L) is generally between 0.0003 and 0.1 and are generally higher than seawater Br/Cl mass ratio (Whittemore, 1995). However, dissolution of halite salts in the soils by

infiltration of precipitation would lower the Br/Cl due to the significantly lower bromide present in halite.

The three most significant ions in the saline water are sodium, calcium and chloride. Reverse cation exchange is thought to be the source of the high calcium as discussed in Chapter Five. Diagrams introduced in Chapter Five showing selected chemical constituents versus chloride indicate sodium, calcium, bromide, and boron are the only ions which show a relationship with chloride concentration. The sum of sodium and calcium versus chloride in meq/L is an almost perfect 1:1 relationship suggesting all the chloride can be accounted for by sodium and calcium. Assuming reverse cation exchange has altered the chemistry of the saline water, the initial source water would have a Na/Cl (meq/L) ratio of 0.94-0.97. This ratio is characteristic of halite and suggests dissolution as the original source of the groundwater salinity. Kaolinite is the dominant clay present within the Speargrass gravels, the cation exchange capacity (CEC) of 3-15 milliequivalents per 100 g is low compared to other clay types (Carroll, 1959; Ma & Eggleton, 1999). However, there is a large volume of kaolinite clay relative to the volume of saline water in the Speargrass gravel, therefore, it is considered plausible that reverse cation exchange has occurred within the valley.

Precipitation in the Wairau Valley would have contained lower sodium and chloride concentrations than the present day during the LGM, this is due to the sea level approximately 120 m lower. The Wairau River would probably have had a similar chemistry to the present day because the catchment geology has not changed over the relatively short time frame (25,000 years). The Wairau River contains approximately 6 mg/L chloride and 5.4 mg/L sodium, this is significant enough that precipitation of evaporites as crystals could have occurred in the vadose zone. Evaporation/dissolution in the vadose zone often results in chemical fractionation as halite will begin to precipitate after calcite anhydrite and gypsum and subsequently the first to dissolve back into solution due to the relative solubility of chloride. This process is common in an arid environment and there is potential for this to have been occurring in the Wairau Valley during the LGM resulting in progressive enrichment of sodium and chloride in the groundwater. Subsequent reverse cation exchange replacing sodium ions in the groundwater for bound calcium. The Br/Cl ratios of the saline waters are low for a fresh water source, however this could be due to chemical fractionation in rain with distance from the ocean. As discusses in

Chapter Five bromide is more soluble than chloride and tends to be incorporated into precipitation more easily than chloride.

6.3.4 Hydrothermal/Metamorphic waters

Due to the proximity of the saline waters to the Wairau Fault it is possible that metamorphic waters have migrated upward from the basement rocks into the valley gravels. The saline waters do not show elevated temperatures (Table 6.2)\, however, there is still potential for hydrothermal saline fluid migration in the past. Taylor (2003) discounted metamorphic water as a source using a Giggenbach plot of the Wairau Valley saline water (Figure 6.9) to infer the water has not had elevated temperatures in the past, however, with extra data now available this potential source is revised.

Table 6.2: Temperature of the saline wells

Well Number	Depth (m)	T^{o}C
O28w/0147	4	18.3
O28w/0147	4	14.8
O28w/0136	35	13.8
O28w/0134	47.2	15.1
O28w/0134	47.2	12.2
O28w/0219	50	15.3
O28w/0219	50	13.6
O28w/0219	50	14.6

South Island hydrothermal waters are predominantly found in active tectonic regions, the majority of hydrothermal springs are associated with the Alpine Fault and Hope Fault. South Island geothermal water is generally low temperature water (40-60^{o}C). The concentration of dissolved solids in the hydrothermal waters generally is a reflection of the rock chemistry that they interact with (Hunt, 1998).

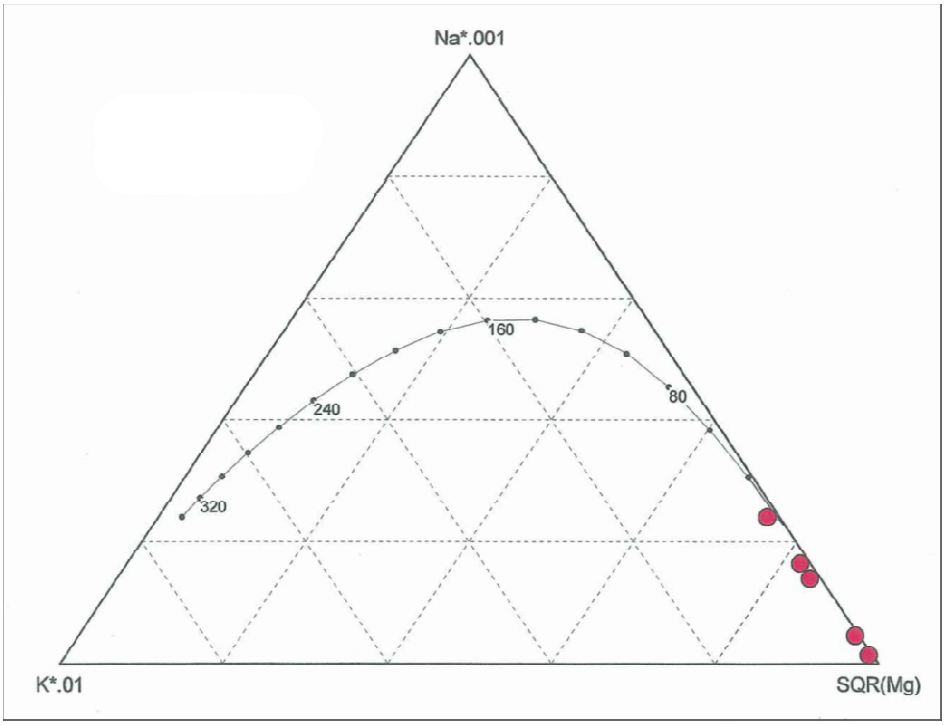


Figure 6.9: Giggenbach plot of saline wells in the Wairau Valley. The trend of the samples suggests the water is not geothermal (Taylor, 2003).

Barnes *et al*., (1978) studied the hydrochemistry of several thermal springs in the South Island of New Zealand, six were situated in the Torlesse terrane and are used in this study as a comparison to the saline water in the Wairau Valley. Appendix 6.1 contains the major ion chemistry of six selected thermal springs in the South Island. All hydrothermal waters showed elevated silica concentrations relative to the Wairau Valley saline water and were approximately in equilibrium with Torlesse Terrane (Figure 6.10). Barnes *et al*., (1978) also identified that the hydrothermal waters had similar $\delta^{18}O$ and δD signatures to meteoric water (Figure 6.11) reflecting a deep circulating meteoric water. South Island hydrothermal waters do not show elevated chloride concentrations and their total dissolved solids concentrations are significantly lower than what is present in the Wairau Valley.

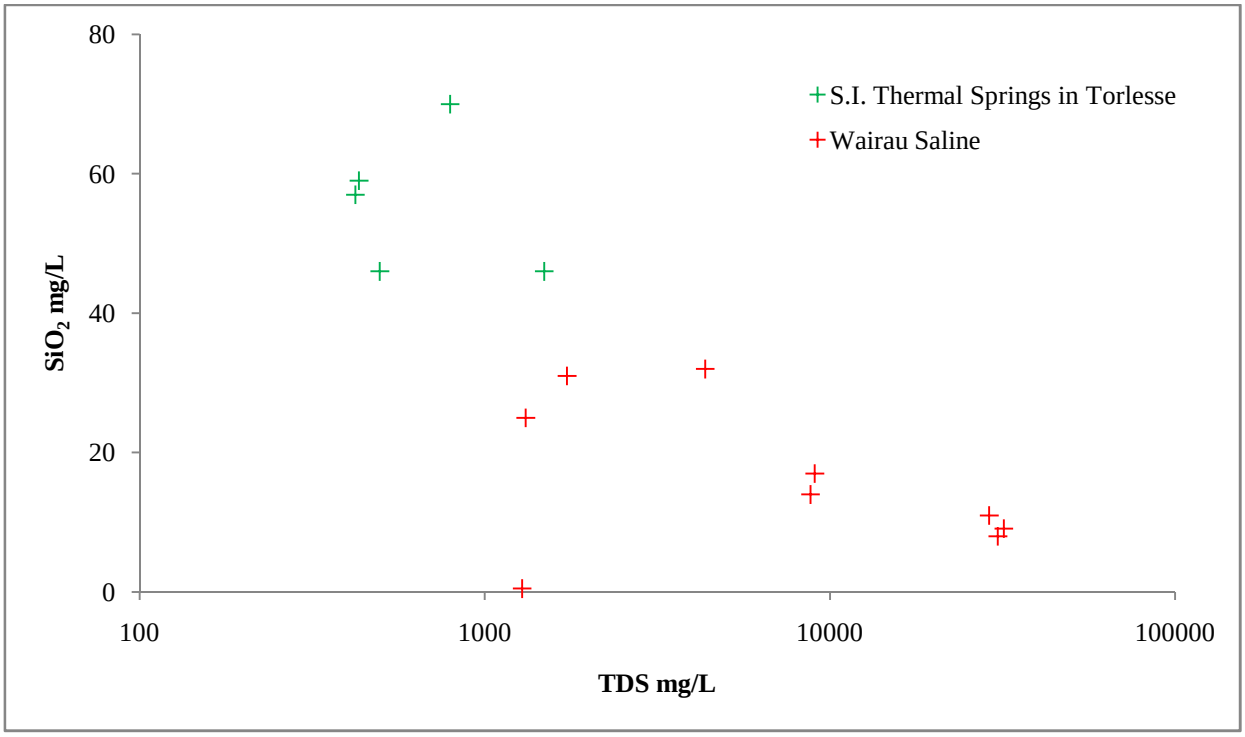


Figure 6.10: SiO_2 versus Total dissolved solids (TDS) for selected South Island springs and Wairau Valley saline waters, thermal water data from Barnes (1978).

Templeton (1998) suggested that metamorphic waters related to the Alpine Fault have $\delta^{13}C$ values between -3 and -8 and $\delta^{18}O$ values between +7 to +12. The low $\delta^{13}C$ value (-26‰) in the most saline well O28w/0219 suggests meteoric water is not mixing with deep metamorphic water.

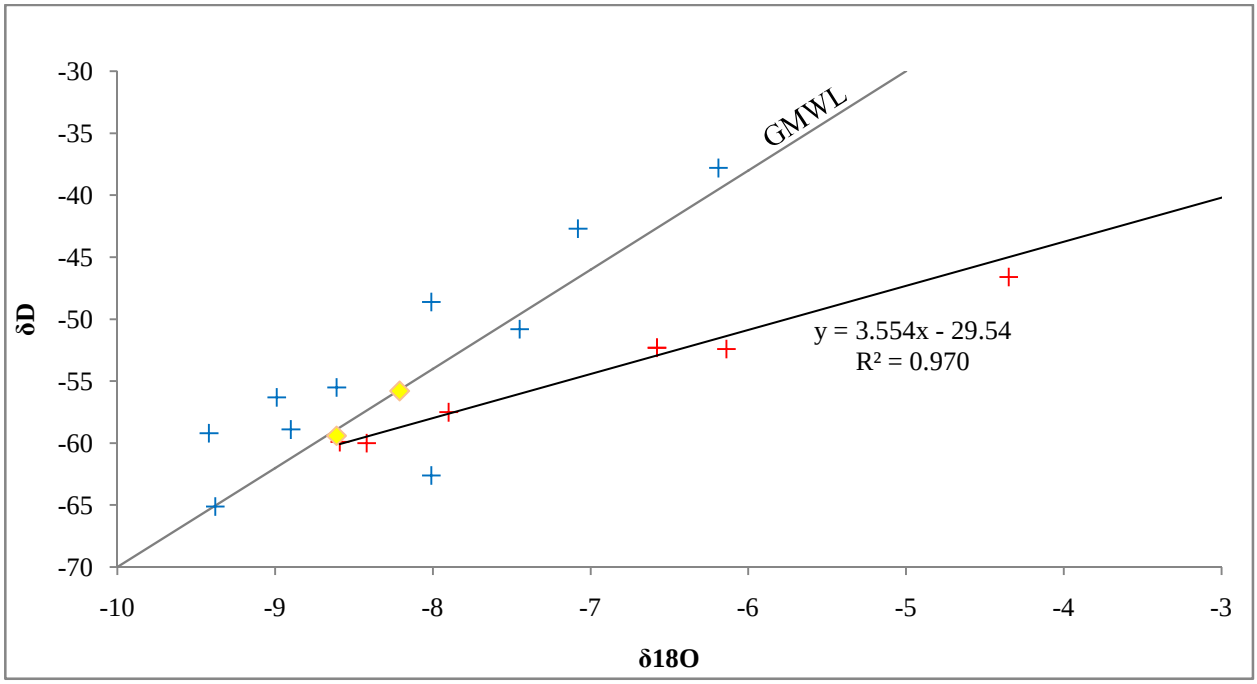


Figure 6.11: δ18O versus δD for saline Wairau Valley wells (red cross) and thermal waters in the South Island (blue cross).

Figure 6.10 shows the silica concentrations versus total dissolved solids for selected South Island thermal waters and Wairau Valley saline water samples. The solubility of silica increases with temperature, therefore, is often used in geothermal groundwater studies (Hem, 1992). Wairau Valley water clearly has lower silica concentrations compared to the geothermal water despite having significantly higher dissolved solids.

The $\delta^{13}C$ value, $\delta^{18}O$ versus δD, and silica concentrations of the saline water suggest that metamorphic waters are not related to the salinity inn the Wairau Valley.

6.3.5 Rock Weathering

Several studies in the literature have shown the natural evolution of groundwater from Ca-Mg-HCO_3 type to Na-SO_4-Cl water over increasing length of flow path and residence time (Chebotarev, 1955; Edmunds *et al*., 1982; Manzor ,1997). The evolution of groundwater is dependent on the minerals available in the groundwater system. Deep groundwater in the Wairau Valley has a very low hydraulic conductivity and is very old. It is possible that over time the salinity of the deep groundwater in the Wairau Valley is derived solely through water rock interaction with the aquifer gravels. The gravels that fill the Wairau Valley almost completely

consist of Torlesse derived sandstone with minor fraction of schist and conglomerate clasts. Both the clasts and the fine matrix are almost entirely quartz and albite. The clay within the matrix has been defined in this study (Chapter Two) to consist entirely of kaolinite probably from the breakdown of Na-feldspars. X-Ray diffraction (XRD) analysis of clast and matrix samples collected during extension of O28w/0219 showed no traces of chloride bearing minerals. X-ray fluorescence analysis by Roser *et al.*, (1995) show that the sandstones and argillite of the Torlesse Terrane in New Zealand contain no appreciable quantities of chloride.

Other rocks in the Wairau Valley but outside the study area which may contribute to the groundwater salinity include the Marlborough greenschist within the Caples Terrane and the Dun Mountain-Matai Terrane. The Caples Terrane contains no significant quantities of chloride (Mortimer & Little, 1998). The ultramafics within the Wairau Valley consist of harzburgite and dunite which both consist predominantly of olivine. Harzubrgite also has associated clinoamphibole, orthopyroxene, and biotite. None of these minerals contain chloride with the exception of biotite which can substitute the OH^- for Cl^-. However, biotite concentrations are low in the Dun Mountain terrane and probably not significant enough to produce the concentrations present in the saline groundwater

The $\delta^{18}O$ versus δD plot suggests that the salinity is not derived from water rock interaction. The characteristic trend for groundwater interaction with aquifer rocks is a horizontal line reflecting ^{18}O enrichment of the groundwater with no hydrogen fractionation occurring (Faure & Mensing, 2005). Isotope exchange reactions with rock require very long residence times and predominantly occur in geothermal environments where the temperature will act as a catalyst for the fractionation process. The apparent correlation between $\delta^{18}O$ and chloride (Figure 6.8). Suggests that chloride is not derived from leaching of salts from old shale and other sedimentary rocks of marine origins. Leaching salts do not alter the stable isotopic composition of a fluid (Payne, 1988).

6.4 Source of the High Salinity

Hydrochemical analysis suggests that metamorphic/hydrothermal water and water/rock interaction processes cannot account for the high salinity in the Wairau Valley. Fault derived formation water or evaporation and dissolution within the Wairau Valley are the most probable

sources of the high salinity, however all the data does not fit to either source completly. Oxygen and hydrogen isotope fractionation data is indicative of an evaporative concentration of Wairau River water, this is supported by the $\delta^{13}C$ value which suggests a terrestrial source. If the approximate age of the groundwater is correct, evaporative concentration is plausible in an arid setting in the Wairau Valley. However, it is possible that solutes and fluid have different origins, this is common in saline formation waters found in other parts of the world (Richter & Kreitler, 1993). The hydrochemistry of the Wairau Valley saline waters is very similar to other formation water which are derived from a seawater source. High sodium calcium, chloride and bromide with low concentrations of sulphate due to sulphate reduction are characteristic of formation waters. The Relationship between chloride and ^{18}O and $\delta^{18}O$ versus δD is difficult to explain although not uncommon in deep saline waters.

The chemical constituents of saline formation waters are almost always related to seawater or dissolution of halite beds at depth. It is considered highly unlikely that the Torlesse terrane could contain seawater from its time of deposition, and it is also does not have associated beds of disseminated halite. Furthermore, the relationship to chloride and ^{18}O suggest simple dissolution of halite cannot be the source. Na-Cl-Br diagrams preclude evaporative enrichment of seawater as the source of the chemical constituents. More analysis of the hydrochemistry is needed to define the source of the elevated salinity in the Wairau Valley any further.

CHAPTER SEVEN

SUMMARY AND FUTURE RECOMENDATIONS

7.1 Thesis Summary

7.1.1 Hydrostratigraphy

The Speargrass gravels which fill the Wairau Valley have a lower permeability compared to the thin layer (approximately 15-20 m) of reworked Speargrass gravels below the Wr 1 terrace surface, this reworked layer defines the Wairau Valley Aquifer. Conductivity at well O28w/0219 increases sharply at approximately 17 m and show some variation to 25 m where conductivity is consistently greater than 5,000 mS/m. Static water levels measured at varying depths during extension of well O28w/0219 suggest gravity drainage is occurring in the valley, however, due to the nature of fluvial deposits natural variations may occur.

Minerals present in the Wairau Valley gravels as identified by XRD analysis include quartz and albite, trace concentrations of mica is also present in one of the samples. Kaolinite was the only clay identified in the samples analysed, probably sourced from the weathering of feldspars.

The Wairau Fault acts as a semi-permeable barrier to groundwater flow and compartmentalises the valley groundwater system. North of the Wairau Fault the upper terrace (Wr 2) groundwater system is controlled buried northeast trending channel deposits. Southern Hills groundwater is thought to traverse the Wairau Fault where these channels intersect with the fault trace. It is not known where this actually occurs in the study area although it is probably related to Excell and Huddleston stream groundwater, Walkers Stream may also contribute, however, a water loss survey would need to be completed to evaluate this possibility.

The Wairau Valley Aquifer below the lower terrace surface (Wr 1) is not recharged by losing reaches in south bank streams, and therefore must be recharged by Southern Hills groundwater. Boundary Creek is considered the most significant source for this groundwater, It loses all

stream flow for most of the year to groundwater upon reaching the valley floor. Bounday Creek has washed out sections of the Wairau Fault and Major terrace riser between Wr 1 and Wr 2 terrace surfaces. This reworked gravel related to Boundary Creek is considered the conduit for significant groundwater flow to cut across the generally north east trending groundwater system to reach the Wairau Valley Aquifer.

7.1.2 Multi-Electrode Resistivity

Three Multi-Electrode resistivity (MER) surveys were completed in the study area. The aim was to identify the extent of the saline groundwater and the depth to saline groundwater. The MER investigations focus on the Mill Road and Parsons Road cross section (survey lines 1 and 2). This was chosen because elevated conductivities had been identified at the surface at the end of Parsons Road between the Southern Hills and the trace of the Wairau Fault, and the highest chloride concentrations had been measured in the 50 m well O28w/0219 which is located along Mill Road on the lower terrace surface (Wr 1). Survey Line 3 was completed to fill a gap in the dataset of survey line 2 and to give a three dimensional model of the groundwater salinity below the Wr 2 terrace surface.

Survey line 1 clearly defines the thickness of the Wairau Valley Aquifer along Mill Road. Below a depth of 20 m very saline groundwater is considered to control the resistivity of the subsurface and in conjunction with the lithological log and hydrochemistry at well O28w/0219 high salinity groundwater was shown to be ubiquitous at depth. Below the Wr 2 terrace surface Survey lines 2 and 3 show very similar profiles. Depth to salinity was variable, north of the Wairau Fault buried channels control groundwater flow. The hydraulic conductivity of the gravels is thought to be a significant factor on the salinity of the groundwater. South of the Wairau Fault, depth to saline groundwater is shallower relative to the rest of the valley, this is thought to be due to the Wairau Fault holding up groundwater flow. Both survey lines 2 and 3 show a potential saline plume originating from depth, immediately south of the Wairau Fault, however, without ground control south of the Wairau Fault it is difficult to draw any firm conclusions from this.

7.1.3 Isotope Analysis

Analyses of stable and radioactive isotopes for saline well O28w/0219 are compared to previous work by Taylor (2003) on the saline groundwater in the Wairau Valley. Stable isotope analysis included hydrogen, oxygen and, carbon and aimed to better define the source of the saline fluid.

Stable isotope analysis saline waters in the Wairau Valley study area are clearly related. The regression line for $\delta^{18}O$ versus δD fits within the slope characteristics of kinetic fractionation by evaporation, chloride does show positive enrichment relative to $\delta^{18}O$ values.

The $\delta^{13}C$ value of -26‰ for the sample at O28w/0219 suggests that the saline water is probably not seawater in origin but derived from a terrestrial setting. The highly negative $\delta^{13}C$ value for the most saline well suggests that the regression between $\delta^{18}O$ and δD cannot be controlled by mixing and the saline groundwater is probably entirely meteoric in origin. However, the source of the fluid may not reflect the source of the solutes.

The ^{14}C groundwater sample collected from well O28w/0219 contained extremely low percent modern carbon value and an estimated age is given at 25,000 years B.P., however, due to the variable chemistry and only one sample at present it is difficult to constrain the age with any certainty. Assuming this age is correct the paleo physiographic setting of the Wairau Valley at this time suggests that the salinity could be entirely derived from concentration through evaporation of meteoric waters. This hypothesis fits well with the stable isotope data, however, more ^{14}C samples are required to accurately define the age of the saline water.

7.1.4 Hydrochemistry

The saline groundwater contains elevated concentrations of sodium, calcium, potassium, magnesium, iron, chloride, bromide, manganese, arsenic, and boron relative to Wairau River and Southern Hills water. Saline samples are very low in sulphate and fluoride. Concentrations of sodium, calcium, and bromide are thought to be related to chloride due to the strong correlation each ion has relative to the chloride concentration. Elevated iron, manganese, and boron with very low sulphate are thought to reflect strongly reducing conditions.

Southern Hills streams show sodium bicarbonate to no dominant type with the exception of Walkers stream which is sodium chloride type which is related to surface runoff of saline water at Homelands. Boundary Creek plot closest to Wairau River water on a trilinear piper diagram. This is due to the sampling location. Boundary Creek is sampled away from the Wairau Valley Floor and has not been altered by local contamination. There is a general stratification of facies types with sodium chloride dominant at depth and no dominant water predominantly shallower than 13-20 m. However, shallow wells close to the fault trace (O28w/0147 and O28w/0117) are identified as sodium chloride facies type.

7.1.5 Source of the Saline groundwater

Metamorphic/hydrothermal waters and water/rock interaction are discounted as potential sources for the Wairau Valley salinity. Two sources which are considered to fit the data the best include; fault derived formation water and evaporative concentration of fresh water within the valley during the Last Glacial Maximum (LGM). Stable isotope data fits well with evaporative concentration and the paleo physiographic setting of the Wairau Valley during the LGM suggests this is a plausible source of the salinity. The salinity is dominated by sodium, calcium, and chloride ions. The high calcium concentrations are considered to result from reverse cation exchange after infiltration of the saline water indicating that the major component of the initial water is sodium chloride. This could be sourced from salt dissolution through infiltration as water moves through the vadose zone. Chemical fraction would concentrate the sodium and chloride ions relative to other evaporite minerals (calcite, anhydrite). Evaporation of water within the vadose zone is common in arid environments and could produce the $\delta^{18}O$ versus δD regression. If saline water was source from within the valley is likely that both evaporative concentration and salt dissolution during infiltration are both occurring. Hydrochemical analysis of the Saline water shows similarities of the Wairau Valley saline water with formation waters found in other parts of the world.

While the saline water is probably is sourced from depth, it is unlikely that this is related to connate waters derived from Torlesse Terrane due to the age and history of the Torlesse. Furthermore connate waters would be expected to be found in other locations in the South Island if derived from Torlesse terrane. There is potential for old seawater infiltration into the Wairau

Fault in the past when the coastline was further inland, however, this would require complete replacement of the initial fluid by an evaporated meteoric water.

7.2 Further Work

Summarised below are the recommendations for future investigations to further define the hydrogeological system of the south bank and the nature of the saline groundwater.

7.2.1 South Bank Hydrogeological System

- Comprehensive stream gauging survey extended from the one completed in this investigation to include Excell and Huddleston reaches prior to losing surface flow. Also include Walkers stream as this is probably has a losing reach to some degree between reaching the valley floor and the Wairau Fault. The same survey should be completed several times throughout the year

- Further chemical sampling of Excell Stream, Huddleston Stream, and Boundary Creek before reaching the valley floor to better define any change in the chemistry of shallow groundwater south of the Wairau Fault.

- Seismic survey at the Mill Road cross section to define the presence of any splay faults and their potential influence on the groundwater flow. A seismic profile may also give a continuous profile of the depth to basement from the Southern Hills to the Wairau River and image the fault within the basement.

- Drill at least one shallow well close to Boundary Creek and complete pump tests on each new well to define the potential for groundwater flow and to determine flow direction. Wells either side of the fault trace would potentially yield the most significant data.

7.2.2 Saline Groundwater

- Further chemical analysis of all saline wells but primarily of well O28w/0219 to attempt to resolve the variations in the chemistry in the present sample set. This is important particularly for bromide concentrations to constrain the source and also the dissolved inorganic carbon to improve on the age of the saline groundwater.

- Collect ^{18}O and D samples from the saline wells to further define the regression between the two isotopic ratios

- Collect samples for ^{13}C analysis from the saline wells (O28w/0134, O28w/0136, O28w/0147, and O28w/0219) to define any potential trends to further define the salinity source. Plotting $\delta^{13}C$ versus $\delta^{18}O$ can identify possible mixing trends.

- Another ^{14}C sample from O28w/0219 to attempt to constrain the age with a reasonable degree of certainty. This should only be completed once the hydrochemistry is stable.

- Complete a Time domain electromagnetic (TEM) surveys in the valley to define the extent of the saline water in the Valley and potentially depth to basement.

- Drill a deep exploration well south of the Wairau Fault to collect water samples for chemical and isotope analysis and depth profile of the conductivity and static water levels. A pump test should be completed if possible.

- Further exploration wells to northeast and southwest of well O28w/0219

- Extend well O28w/0219 to 80 m and collect samples for stable isotope and hydrochemical analysis.

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